

Sol-gel Synthesis and Functionalization Cascade of Zr-MOF: Tailoring Framework Functionality, Stability, and Catalytic Performance for CO₂ Fixation

Ali Morsali

morsali_a@modares.ac.ir

Tarbiat Modares University

Mohammad Mazraeh

Tarbiat Modares University

Behnam Habibi

Tarbiat Modares University

Sobhan Rezayati

Tarbiat Modares University

Research Article

Keywords: Metal-organic frameworks (MOFs), UiO-66, Chiral, L-alanine, Co-catalyst, Sol-gel method

Posted Date: October 1st, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11215927/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: The authors declare no competing interests.

Abstract

The pressing demand for sustainable carbon utilization has spurred the development of efficient heterogeneous catalysts for the chemical fixation of CO₂ into value-added cyclic carbonates. Despite significant advances in metal-organic frameworks (MOFs), most UiO-66 based catalytic systems still suffer from relatively low catalytic performance and limited selectivity. In this study, a Zr-based MOF, UiO-66 and its L-alanine-functionalized derivative, UiO-66@Ala, were synthesized via a sol–gel method, followed by post-synthetic alkyl-halide functionalization to incorporate bromide ions, yielding UiO-66@Ala/Br[−]. UiO-66@Ala afforded 99% conversion of styrene oxide to styrene carbonate in the presence of tetrabutylammonium bromide (TBAB) as a cocatalyst under solvent-free conditions, whereas UiO-66@Ala/Br[−] achieved 61% conversion without the addition of any external cocatalyst. Complete characterization (PXRD, FT-IR, ¹H NMR, BET, TGA/DTG, EDX, XPS and CD) confirms successful incorporation of the chiral L-alanine linker, retention of the UiO-66 topology and high stability. Analysis after the reaction confirms structural integrity and retention of chirality. Sequential functionalization progressively transformed the UiO-66 framework from a pristine Zr-based platform into a chiral L-alanine-functionalized catalyst and, upon further post-synthetic modification, into a framework incorporating Br[−] nucleophiles, demonstrating how functionalization can tune the chemical environment and catalytic behavior of the MOF. Overall, this work establishes a sol–gel-derived and systematically functionalized UiO-66 platform for correlating progressive structural and chemical modification with framework stability and catalytic performance, providing a versatile strategy for the development of multifunctional MOF catalysts for CO₂ fixation.

Introduction

The substantial increase in anthropogenic greenhouse gas emissions, particularly carbon dioxide (CO₂), since the onset of the Industrial Revolution has become one of the principal drivers of global climate change and environmental degradation.¹ The extensive consumption of fossil fuels, together with emissions from industrial activities and transportation, has resulted in a continuous rise in atmospheric CO₂ concentrations, intensifying the greenhouse effect and posing serious ecological and socioeconomic challenges.² Consequently, the development of sustainable and efficient strategies for mitigating anthropogenic CO₂ emissions has emerged as a global scientific priority. Beyond its role as a greenhouse gas, CO₂ represents an abundant, inexpensive, non-toxic, and renewable C1 carbon feedstock with considerable potential for the synthesis of value-added chemicals and fuels.³ In particular, extensive efforts have been devoted to the activation and transformation of thermodynamically stable CO₂ into high-value products, demonstrating its potential as an environmentally benign carbon source for the production of a wide range of fine chemicals and functional materials.⁴ Over the past decades, numerous homogeneous and heterogeneous catalytic systems have been developed for the cycloaddition of CO₂ with epoxides to produce cyclic carbonates.⁵ Although homogeneous catalysts, including ionic liquids,⁶ Schiff bases,⁷ and some complexes,⁸ often

exhibit high catalytic activity. However, for some homogeneous catalysts, their practical application is hindered by difficult product separation and poor recyclability.⁹ In contrast, heterogeneous catalysts offer superior recoverability and operational stability but frequently require elevated temperatures, co-catalysts, or organic solvents to achieve satisfactory performance.¹⁰ Consequently, the development of efficient, recyclable heterogeneous catalysts capable of operating under mild reaction conditions remains a major objective.^{11, 12} Research suggests that an optimal heterogeneous catalyst for the cycloaddition of CO₂ with epoxide should exhibit a large surface area, selective CO₂ adsorption, adequate Lewis/Brønsted acidic or basic sites for substrate activation, and high stability. It is imperative to establish robust frameworks utilizing Lewis acidic metal ions for the effective coupling of CO₂ with epoxides, considering these factors.¹³

MOFs, as promising materials, can have a major impact on catalytic organic transformations due to their high porosity and desirable architectural engineering.¹⁴ Due to this highly desirable engineering, their applications are not limited to catalytic organic transformations but also include extensive use in photocatalysis,¹⁵ electrocatalysis,^{16, 17} separation,¹⁸ and medicine.¹⁹ Zr-based MOFs demonstrate considerable suitability for this application owing to their robust stability across a broad spectrum of pH conditions, facile functionalization capabilities via diverse synthetic approaches, and the capacity to precisely control their porosity and surface area through judicious selection of constituent building blocks or the implementation of defect engineering methodologies.²⁰ For instance, UiO-66 composed of zirconium in nodal positions and terephthalic acid ligands exhibits substantial stability and preserves its Lewis acidity. Its properties make it a highly suitable candidate for catalytic applications.²¹ Considering the insights gained from prior reports, it is evident that multiple variables and alterations can influence the CO₂ fixation process. The integration of metallic nodes (possessing Lewis/Brønsted acidic characteristics) alongside basic functional moieties, such as amine groups within organic linkers, proves efficacious for cycloaddition reactions. In this context, the metallic nodes serve to activate epoxides, whereas the carbon dioxide primarily undergoes activation by the basic sites.²² Lewis acid-based MOF catalysts incorporating basic functional groups represent promising heterogeneous catalysts for organic transformations. It has been determined that the incorporation of NH₂-functionalized linkers led to enhanced basicity and catalytic performance in these MOF architectures. Fundamentally, the catalytic reactions occurred as a result of the cooperative effect between Lewis acid metal nodes located at proximate basic sites on the MOF's pore surface, ultimately yielding bifunctional acid-base heterogeneous catalysts.²³ Sol-gel processing has emerged as a versatile approach for the synthesis and functionalization of MOF-based materials, in which molecular precursors undergo hydrolysis, condensation, and subsequent network formation to generate a three-dimensional gel structure that can evolve into the final porous framework. In particular, sol-gel strategies have been successfully applied to Zr-based MOFs, including UiO-66, HKUST-1, ZIF-8, enabling the incorporation of different functional ligands and the controlled development of framework structures and properties.²⁴⁻²⁶

Beyond the selection of functionalized linkers and effective metal nodes, the utilization of an effective co-catalyst is of critical significance for CO₂ fixation, specifically in its role as a ring-opening agent.²⁷ Moreover, the integration of chirality, an inherent property of the natural world, is of significant consequence in catalytic disciplines, including CO₂ fixation, to achieve enhanced selectivity. The significance of chiral metal-organic frameworks (CMOFs) has escalated in recent years, owing to their distinctive properties. Chiral MOFs can be synthesized through two primary approaches: direct synthesis and post-synthesis. Optimization efforts concerning chiral MOFs are currently extensive. This phenomenon is largely a consequence of their adeptness in refining pore geometry and magnitude, which is determined by their topological framework, a discipline referred to as reticular chemistry. In addition, the characteristic of a chiral environment combined with the considerable internal surface area generates high expectations for MOFs.²⁸

Herein, the incorporation of individual modifications into UiO-66 can offer distinct advantages while also introducing specific limitations, as systematically summarized in Fig. 1. Specifically, the integration of L-alanine as a functionalized linker, offering both readily available -NH groups and a chiral environment, is a promising approach for optimizing the chemical environment of UiO-66 for effective catalytic CO₂ fixation. Consequently, two UiO-66-based catalysts featuring these functionalities were deliberately designed to establish durable and effective catalytic systems: UiO-66@Ala, which requires an external co-catalyst, and UiO-66@Ala/Br⁻, which incorporates the bromide functionality intrinsically and facilitates a co-catalyst-free operation. Comprehensive characterization of both materials was performed via FT-IR spectroscopy, PXRD, ¹H NMR spectroscopy, BET, TGA/DTG, EDX, CD, and XPS to elucidate their overall properties. UiO-66@Ala, a mixed-linker UiO-66 architecture, offers accessible -NH sites and a chiral environment. When combined with TBAB as an external co-catalyst, it facilitates highly efficient CO₂ cycloaddition, achieving up to 99% styrene oxide conversion under optimized conditions. Furthermore, UiO-66@Ala/Br⁻ retains the essential structural and functional aspects of UiO-66@Ala, with the bromide functionality integrated into the catalytic structure, thus negating the need for an external co-catalyst. Moreover, UiO-66@Ala/Br⁻ displays enhanced catalytic capabilities, achieving 61% conversion in the CO₂ fixation reaction. After operation, characterization via FT-IR, PXRD, XPS, and CD confirms that both catalysts remain largely intact structurally following the CO₂ fixation. The continued presence of crucial functional groups and chiral features underscores their significant operational stability. The catalyst's effectiveness stems from its integrated design: Zr⁴⁺ sites act as Lewis acids for epoxide activation, while -NH groups offer Lewis basicity, aiding substrate interaction and reaction advancement. Also, the chiral environment provided by L-alanine might affect the immediate reaction surroundings and the selection of products, with the embedded Br⁻ entities potentially functioning as efficient nucleophiles for ring-opening. By integrating these functions into one porous structure, a cooperative catalytic platform is formed, enabling Lewis acid activation, nucleophilic ring opening, chiral microenvironment engineering, and CO₂ insertion to work together.

Experimental Section

Materials and methods

All solvents and materials were received and used without further purifications. FT-IR, PXRD, TGA/DTG, N₂ adsorption-desorption, ¹H NMR, EDX, XPS, and circular dichroism (CD) measurements were performed using the instruments described in the Supporting Information. Catalytic conversions were determined by gas chromatography (GC) and further analyzed by ¹H NMR spectroscopy.

Synthesis and Functionalization of UiO-66

UiO-66 and L-alanine-functionalized UiO-66 (UiO-66@Ala) were synthesized through a sol–gel route based on previously reported procedures with slight modifications.^{29, 30} Briefly, ZrCl₄ and acetic acid were dissolved in DMF, followed by the controlled addition of water under vigorous stirring. In parallel, H₂BDC was dispersed in DMF, and the two solutions were subsequently combined and subjected to thermal treatment to induce gel formation, followed by static aging. (**Figure S1**) The resulting solid was isolated, washed sequentially with water, ethanol, and acetone, and dried to afford UiO-66. UiO-66@Ala was prepared under identical conditions using an equimolar mixture of H₂BDC and L-alanine as the organic components.

UiO-66@Ala/Br[−] was subsequently prepared by post-synthetic modification of UiO-66@Ala. The functionalized framework was dispersed in DMF, followed by the dropwise addition of a DMF solution of methyl bromide under continuous stirring at room temperature. The stirring continued for 24 h. The resulting solid was thoroughly washed and dried to afford UiO-66@Ala/Br[−].

CO₂ cycloaddition reactions were performed under solvent-free conditions using predetermined amounts of epoxide and catalyst, with TBAB added as a co-catalyst where applicable, under a CO₂ atmosphere. Conversion was determined by GC and ¹H NMR spectroscopy, with detailed reaction conditions provided in the Supporting Information.

Result and Discussion

Structural Characterization

UiO-66 and UiO-66@Ala was successfully synthesized through a straightforward sol-gel method,^{29, 30} whereas UiO-66@Ala/Br[−] was subsequently obtained via post-modification of the UiO-66@Ala catalyst (Fig. 2a). Detailed synthetic procedures are provided in the Supporting Information. The successful formation of the synthesized materials was further verified by EDX elemental mapping. As shown in **Figures S2-S4**, the elemental distribution confirms the homogeneous presence of Zr, C, O, and N within the UiO-66@Ala framework, while the incorporation of Br in UiO-66@Ala/Br[−] verifies the successful post-synthetic functionalization of the parent MOF. Furthermore, the chemical structures of UiO-66, UiO-66@Ala and UiO-66@Ala/Br[−] were further investigated by FT-IR spectroscopy, and the corresponding

spectra are presented in **Figure S5-S6**. A broad absorption band centered at 3200–3400 cm^{-1} is attributed to the stretching vibration of the -NH groups.^{31, 32} The characteristic absorption bands observed in the range of 1250–1700 cm^{-1} correspond to the stretching vibrations of C = O, C = C, C-N, and N-H bonds, confirming the coordination of ligands with the nodal positions within the MOF framework.³² In addition, the absorption peak located at 2931 cm^{-1} is assigned to the stretching vibration of aliphatic C-H (sp^3) bonds, which serves as another characteristic feature of the synthesized frameworks. Comparative analysis of the FT-IR spectra for UiO-66@Ala and UiO-66@Ala/ Br^- revealed minor spectral shifts, confirming successful structural modification while preserving the integrity of the parent UiO-66 framework. PXRD analysis was performed to investigate the crystallographic structures of UiO-66, UiO-66@Ala, and UiO-66@Ala/ Br^- . The experimental diffraction patterns are in excellent agreement with the reported simulated patterns of UiO-66 type frameworks, confirming the successful formation of the desired crystalline structures.^{33, 34} The PXRD pattern of UiO-66@Ala exhibits characteristic diffraction peaks at 2θ values of 7.3°, 8.48°, 14.72°, 18.64°, 22.24°, and 25.76°, which can be indexed to the (111), (200), (222), (420), (511), and (600) crystallographic planes, respectively, together with several additional reflection characteristic of the UiO-66 framework (Fig. 2b). These diffraction features closely match those of the simulated UiO-66 analogues, further verifying the high crystallinity and phase purity of the synthesized material. Specifically, the diffraction patterns of both UiO-66@Ala and modified UiO-66@Ala/ Br^- correspond to that of the parent UiO-66 framework. This indicates that the underlying crystal structure remains unaltered by either the mixed-linker engineering or the subsequent bromide functionalization. The presented data corroborates the sustained structural integrity and extended crystallinity of the UiO-66 framework following the modification procedure.

To investigate the porosity of the synthesized materials, nitrogen adsorption-desorption measurements were performed, and the corresponding BET surface areas were determined for UiO-66, UiO-66@Ala, and UiO-66@Ala/ Br^- . As shown in Fig. 3a, UiO-66@Ala exhibits a specific surface area of 805.55 $\text{m}^2 \text{g}^{-1}$, whereas the modified UiO-66@Ala/ Br^- displays a reduced surface area of 575.83 $\text{m}^2 \text{g}^{-1}$ (Fig. 3b). Comparing to the pristine UiO-66, the noticeable decrease in the BET surface area of functionalized UiO-66 samples following bromide functionalization can be attributed to the partial occupation of the pore channels and active adsorption sites by the introduced bromide moieties, thereby reducing the accessible pore volume and surface area. (**Figure S7**) This observation provides additional evidence for the successful modification of UiO-66@Ala and is in excellent agreement with the results obtained from FT-IR, PXRD, and elemental analyses. Collectively, these findings demonstrate that although the functionalization process decreases the accessible porosity, the crystalline framework of the UiO-66 structure remains well preserved, confirming the successful construction of UiO-66@Ala/ Br^- . ^1H NMR spectroscopy was employed to verify the successful incorporation of the primary linker, terephthalic acid, together with the L-alanine functional ligand within the UiO-66 framework. Prior to analysis, the MOF samples were chemically digested following the $\text{D}_2\text{O}/\text{NaOH}$ protocol, (**Scheme S1**) and the detailed digestion procedure is described in the Supporting Information.³⁵ As presented in **Figures S8-S9**, the characteristic proton resonances corresponding to both BDC^{2-} and L-alanine are clearly observed,

confirming the successful incorporation of the functional ligand into the framework. Moreover, the retention of the characteristic signals associated with BDC²⁻ indicates that the parent UiO-66 architecture is largely preserved following mixed-linker construction. These results provide strong molecular-level evidence for the successful integration of L-alanine into UiO-66@Ala, further supporting the conclusions drawn from the complementary structural characterization techniques such as PXRD, FT-IR, and elemental mappings. The thermal stability and decomposition behavior of UiO-66@Ala and UiO-66@Ala/Br⁻ were investigated by TGA/DTG, and the corresponding thermograms are presented in Figs. 3c and 3d. Both materials exhibit similar thermal decomposition profiles to the pristine UiO-66, (**Figure S10**) demonstrating the excellent thermal stability characteristic of UiO-66-based frameworks. The initial weight loss observed below approximately 350 °C is primarily attributed to the removal of physically adsorbed and coordinated solvent molecules, followed by the dehydroxylation of the Zr₆-oxo clusters and the elimination of residual modulator species incorporated during synthesis.³⁵ At higher temperatures, between 500 and 600 °C, rapid framework decomposition occurs as a result of the breakdown of the organic linkers, ultimately leading to the collapse of the MOF architecture.³⁶ Following complete decomposition, both materials retain approximately 45–50 wt% residue, which is mainly associated with the formation of thermally stable zirconium oxide species. Overall, the TGA/DTG results confirm that both UiO-66@Ala and UiO-66@Ala/Br⁻ possess high thermal stability, indicating that neither mixed-linker engineering nor bromide functionalization adversely affects the intrinsic thermal robustness of the UiO-66 framework. Furthermore, the incorporation of L-alanine as a chiral functional ligand within the UiO-66 framework is expected to impart chirality to the resulting materials. To verify the successful transfer of chirality, CD spectroscopy was performed for both UiO-66@Ala and UiO-66@Ala/Br⁻, and the corresponding spectra are presented in **Figure S11**. For comparison, the CD spectrum of pure L-alanine is also included. Both functionalized MOFs exhibit characteristic Cotton effects within the spectral region associated with L-alanine, demonstrating that the chiral environment of the amino acid is retained after its incorporation into the framework. These observations provide strong evidence that the chirality of L-alanine is successfully transferred to the UiO-66 architecture, confirming the formation of chiral MOF materials. Moreover, the preservation of the chiroptical response following bromide functionalization indicates that the modification process does not compromise the chiral nature of the framework. Collectively, the CD results further corroborate the successful incorporation of L-alanine and the construction of chiral UiO-66@Ala and UiO-66@Ala/Br⁻ catalysts.

XPS analysis was employed to investigate the surface elemental composition and chemical states of the constituent elements in UiO-66@Ala. As shown in **Figure S12**, the XPS survey spectrum confirms the presence of Zr, C, O, and N, consistent with the successful incorporation of the L-alanine functionality into the UiO-66 framework. The Zr 3d spectrum in Fig. 4a displays two characteristic peaks centered at 182.68 and 185.03 eV, which can be assigned to the Zr 3d_{5/2} and Zr 3d_{3/2} components, respectively. The corresponding binding energies are consistent with the presence of Zr⁴⁺ species within the zirconium-oxo clusters of the UiO-66 framework.³⁷ The O 1s spectrum (Fig. 4b) further reveals the characteristic oxygen environments associated with the framework, including contributions from Zr-O bonds and carboxylate oxygen species originating from the organic linkers.³⁸ In addition, the C 1s spectrum

(Fig. 4c) exhibits signals attributable to C-N and O-C = O environments, corresponding to the amino-functionalized linker and carboxylate groups, respectively, thereby supporting the successful incorporation of L-alanine into the MOF architecture. Finally, the N 1s spectrum (Fig. 4d) indicates the presence of nitrogen species associated with -NH_2 and protonated -NH_3^+ functionalities within UiO-66@Ala. These nitrogen-containing environments can be reasonably attributed to the L-alanine-derived functionality incorporated into the framework. The coexistence of neutral and protonated nitrogen species may arise from the coordination environment and post-synthetic proton-transfer processes involving the amino functionality. Such protonation behavior has also been reported for amino-acid-functionalized materials, where modification and coordination processes can generate different nitrogen chemical states, including protonated ammonium species.^{32, 39}

For UiO-66@Ala/ Br^- , the XPS survey spectrum reveals the presence of Zr, C, O, N, and Br, providing evidence for the successful incorporation of the bromide functionality while preserving the fundamental chemical composition of the UiO-66@Ala framework (**Figure S13**). The Zr 3d spectrum shown in Fig. 5a displays two characteristic components centered at 182.62 and 184.88 eV, which can be assigned to the Zr $3d_{5/2}$ and Zr $3d_{3/2}$ states, respectively. These binding energies are consistent with the presence of Zr^{4+} species within the zirconium-oxo clusters of the UiO-66 framework.^{28, 37} The O 1s spectrum (Fig. 5b) exhibits contributions corresponding to the distinct oxygen environments within the framework, particularly Zr-O species and carboxylate oxygen atoms associated with the organic linkers.³⁸ Furthermore, the C 1s spectrum (Fig. 5c) contains characteristic contributions attributable to C-N and O-C = O environments, which can be assigned to the amino-containing functionality and carboxylate groups, respectively.⁴⁰ The N 1s spectrum (Fig. 5d) further demonstrates the presence of several nitrogen-containing chemical environments, including -NH_2 , -NH- , and protonated -NH_3^+ species, indicating the retention of the L-alanine-derived functionality within the modified framework.^{32, 40} Importantly, the Br 3d spectrum presented in **Figure S14** provides direct evidence for the successful incorporation and persistence of bromide species within UiO-66@Ala/ Br^- . The binding energies and corresponding chemical assignments obtained from the XPS measurements before and after the CO_2 fixation reaction are systematically summarized in **Table S1**, enabling a direct comparison of the surface chemical states before and after catalytic operation. Collectively, the XPS results, in conjunction with the complementary spectroscopic and structural characterization, support the successful construction of the multifunctional UiO-66@Ala/ Br^- catalytic platform.

CO₂ Fixation Procedure

The catalytic performance of UiO-66@Ala, in the presence of TBAB as a co-catalyst, and UiO-66@Ala/ Br^- , without the addition of any external co-catalyst, was systematically evaluated toward the cycloaddition of CO_2 with epoxides to produce cyclic carbonates. In particular, their catalytic efficiency for epoxide ring opening and subsequent CO_2 insertion was investigated and correlated with their structural and electronic properties. To gain comprehensive insight into the catalytic mechanism and catalyst durability, extensive post-catalytic characterizations were performed, including XPS before and after catalysis to

examine changes in the electronic structure, CD spectroscopy to assess the preservation of chirality, as well as PXRD and FT-IR spectroscopy to evaluate structural stability following the catalytic reaction. Styrene oxide was selected as the model substrate for catalytic CO₂ fixation, and the reaction conditions were optimized at 1 atm CO₂ with a reaction time of 12 h, together with the optimization of other key reaction parameters. Detailed experimental procedures, optimization studies, and catalytic protocols for the CO₂ fixation reaction are provided in the Supporting Information. These comprehensive investigations enable a direct comparison between the co-catalyst-assisted and self-cocatalytic systems while simultaneously elucidating the relationship between catalyst structure, chirality, electronic properties, and catalytic performance.

Following the successful synthesis and comprehensive characterization of UiO-66@Ala as a recyclable and chiral MOF catalyst, our primary objective was to develop an efficient catalytic protocol for the fixation of CO₂ through the cycloaddition reaction of styrene oxide, selected as a model epoxide, to produce the corresponding (R,S) cyclic carbonate (styrene carbonate). To maximize the catalytic efficiency, a systematic optimization of the reaction conditions was performed by investigating the effects of several key parameters, including catalyst loading, co-catalyst (TBAB) concentration, reaction temperature, reaction time, and solvent selection. (Fig. 6) The results of these optimization studies are summarized in **Table S2**. The influence of catalyst loading was subsequently investigated by varying the amount of UiO-66@Ala from 10 to 60 mg (**Table S2, Entries 1–6**). As shown, increasing the catalyst dosage progressively enhanced the conversion of styrene oxide into styrene carbonate owing to the increased availability of accessible catalytic active sites. However, only marginal improvements were observed when the catalyst loading exceeded 30 mg, suggesting that the catalytic system had approached its maximum efficiency under the selected reaction conditions. Therefore, 30 mg was selected as the optimal catalyst loading for all subsequent experiments (**Table S2, Entry 3**). The effect of TBAB was further examined. The combined catalyst/co-catalyst system significantly improved the catalytic performance, and systematic variation of the TBAB amount revealed that 100 mg provided the highest conversion of styrene oxide under 1 atm CO₂ (**Table S2, Entries 7–13**). The influence of solvent polarity and reaction medium was also systematically evaluated using CH₃CN, MeOH, DMF, THF, CHCl₃, and EtOH (3 mL) under otherwise identical reaction conditions (**Table S2, Entries 14–19**). Among the solvents investigated, ethanol under reflux conditions afforded the highest catalytic performance, achieving a styrene carbonate conversion of 97% (**Table S2, Entry 19**). The superior performance observed in ethanol may be associated with its favorable balance of solvent polarity, substrate solubility, and efficient mass transport during the catalytic process. Finally, a control experiment was performed using TBAB alone in the absence of UiO-66@Ala. Under identical reaction conditions, only 28% conversion of styrene oxide was obtained (**Table S2, Entry 20**), demonstrating that the MOF catalyst is the principal active component responsible for efficient CO₂ fixation, while TBAB primarily serves as a cooperative co-catalyst that enhances the overall reaction kinetics. Furthermore, we decided to explore the potential and effectiveness of this approach for the creation of (R,S)-cyclic carbonates after determining the ideal reaction conditions. In order to produce the (R,S)-cyclic carbonates, we looked at

the conversion and selectivity of cycloaddition of CO₂ to various epoxides under solvent-free circumstances at 80°C (**Table S4, method A**).

A similar optimization study was carried out for UiO-66@Ala/Br⁻ under otherwise identical reaction conditions. Compared to the previous catalytic system, no external TBAB co-catalyst was added as bromide species were incorporated in the catalyst framework. **Table S3** summarizes the results of the optimization. Among the conditions investigated, the highest styrene carbonate conversion was achieved using 60 mg of UiO-66@Ala/Br⁻ under solvent-free conditions at 80°C for 24 h, resulting in a conversion of 61%. Under similar conditions, the conversion decreased to 44% with the reduction of the reaction time to 12 h. These results suggest that the immobilized bromide species are involved in the catalytic activity and can be used as an alternative to the externally added homogeneous TBAB co-catalyst. Thus, the application of UiO-66@Ala/Br⁻ allows CO₂ fixation in a simplified, solvent-free catalytic system without the need for additional external bromide source. However, limitation lies within bromide leaching and low conversions, therefore, future works can focus on stabilizing bromide within architectures of MOFs. After establishing the optimal reaction conditions, the substrate scope of the UiO-66@Ala/Br⁻ catalytic system was investigated for the synthesis of a series of cyclic carbonates through the cycloaddition of CO₂ with various epoxides. The conversion of epoxides and the selectivity toward the corresponding cyclic carbonates were evaluated under the optimized solvent-free conditions at 80°C (**Table S4, Method B**). As summarized in **Table S4**, the catalyst efficiently promoted the conversion of a range of terminal epoxides into their corresponding cyclic carbonates. The results demonstrate the applicability of UiO-66@Ala/Br⁻ as a heterogeneous bifunctional catalyst for the solvent-free fixation of CO₂ into value-added cyclic carbonate products.

In addition to the optimization studies, the catalytic performances of several control systems, including ZrCl₄, pristine UiO-66, L-alanine, and a physical mixture of UiO-66 and L-alanine, were evaluated under the optimized reaction conditions to elucidate the individual contributions of the metal precursor, MOF scaffold, and chiral ligand. These catalytic tests were performed using 30 mg of catalyst in the presence of 100 mg of TBAB as the co-catalyst under solvent-free conditions at 80°C and 1 atm CO₂. As summarized in (**Table S5**, see supporting information), UiO-66@Ala and UiO-66@Ala/Br⁻ exhibited markedly superior catalytic activity compared with all control samples, demonstrating that the integration of L-alanine into the UiO-66 framework generates a synergistic catalytic environment that cannot be achieved by the individual components or their physical mixture. To confirm the heterogeneous nature of the catalytic process, hot-filtration tests were carried out for both UiO-66@Ala and UiO-66@Ala/Br⁻ under the optimized reaction conditions (**Figures S15 and S16**). For UiO-66@Ala, the solid catalyst was removed via centrifugation from the reaction mixture at the middle of optimal reaction time, (after 6 h) at which point a styrene carbonate conversion of 62% had been reached. The supernatant was then allowed to react further under identical conditions in the absence of the solid. Upon completion of rest of the reaction time, only a negligible increase in conversion (< 2%) was observed, indicating that no catalytically active species leached into the. An analogous hot-filtration experiment was performed for UiO-66@Ala/Br⁻: after removal of the solid at 12 h (32% conversion), the

filtrate showed only a marginal increase in conversion ($< 1\%$) upon continued reaction, demonstrating that UiO-66@Ala/ Br^- also operates without detectable leaching of active sites. The recyclability and long-term stability of UiO-66@Ala and UiO-66@Ala/ Br^- were also systematically evaluated through consecutive catalytic cycles. As illustrated in **Figure S17 and S18** the catalyst could be readily recovered and reused for five successive reaction cycles, exhibiting only a slight decrease in catalytic activity while maintaining high conversion efficiency. Although UiO-66@Ala/ Br^- maintained high catalytic activity throughout the recycling experiments, the more pronounced decrease in performance observed between the fourth and fifth catalytic cycles is likely attributable to the partial leaching of the catalyst specially in functional groups. This interpretation is further supported by the post-catalytic XPS analysis, which indicates changes in the surface chemical composition consistent with the loss of these functional moieties. Furthermore, the stereochemical characteristics of the obtained cyclic carbonates were investigated using chiral GC. The chromatographic profile of the predominant enantiomer exhibited a strong and well-defined signal, and the obtained enantiomeric distribution was consistent with the results obtained from GC analyses (**Figure S19 and S20**), confirming the reliability of the catalytic system toward the formation of chiral cyclic carbonates. Finally, the molecular structure of the resulting (R,S)-styrene carbonate product mixture was further verified by ^1H NMR spectroscopy (**Figure S21 and S22**), providing additional confirmation of the successful cycloaddition of CO_2 and the formation of the desired cyclic carbonate products.

Electronic Structure, Post-Reaction Characterization, and Proposed Catalytic Mechanism

From a mechanistic perspective (**Figure S23**), the coexistence of these chemically distinct functionalities provides a plausible basis for the observed catalytic activity. The Zr^{4+} centers can function as Lewis acidic sites for epoxide activation, facilitating polarization of the C-O bonds and rendering the epoxide more susceptible to nucleophilic attack. Meanwhile, the amino functionalities can provide complementary Lewis basic interactions and participate in substrate activation and reaction progression. The incorporated Br^- species can serve as accessible nucleophiles for efficient epoxide ring opening, while the chiral microenvironment introduced by L-alanine may further influence the local reaction environment and potentially contribute to product selectivity. Thus, the integration of Lewis acidic Zr^{4+} centers, amino functionalities, nucleophilic Br^- species, and a chiral L-alanine-derived environment within a single porous architecture establishes a cooperative catalytic platform in which epoxide activation, nucleophilic ring opening, CO_2 insertion, and subsequent cyclic-carbonate formation can be effectively unified. Furthermore, results collectively demonstrate the high structural robustness and operational durability of the catalysts under the applied CO_2 fixation conditions over five consecutive catalytic cycles. Post-reaction XPS analysis indicates that the characteristic Zr 3d, O 1s, C 1s, and N 1s signals of both catalysts remain largely preserved after five cycles, with no substantial changes in their corresponding chemical states, supporting the overall chemical and structural stability of the UiO-66 based frameworks (Fig. 7a-d, **Figures S24 and S25**). Nevertheless, a noticeable difference was observed

in the Br 3d region of UiO-66@Ala/Br⁻ after five catalytic cycles. Although the post-catalytic spectrum exhibits increased noise, the Br 3d signal remains detectable, indicating that bromide species are retained within the functionalized framework after repeated catalytic operation. (**Figure S26**) This observation is consistent with the recycling experiments, in which the catalytic conversion remains relatively stable during the initial cycles but decreases more noticeably between the fourth and fifth cycles. The gradual decline in catalytic performance can therefore be reasonably associated with progressive Br⁻ leaching, which reduces the availability of the nucleophilic sites responsible for epoxide ring opening. This bromide leaching represents an important limitation of the present catalyst and provides a clear direction for future studies aimed at developing more strongly anchored or stabilized anionic functionalities within the framework. Further evidence for the structural integrity of both catalysts is provided by FT-IR and PXRD analyses after five catalytic cycles (**Figure S27 and Fig. 7e**). The preservation of the characteristic vibrational features and diffraction patterns indicates that the fundamental UiO-66 framework remains intact after prolonged catalytic operation, in agreement with the post-reaction XPS results. Moreover, CD analysis demonstrates that the chiral characteristics originating from the L-alanine functionality are substantially retained after catalysis (**Figure S28**). However, UiO-66@Ala/Br⁻ exhibits a noticeable attenuation of its CD response after repeated operation, attributed particularly to the final cycles. Overall, the combined XPS, FT-IR, PXRD, and CD analyses indicate that the UiO-66-based architecture exhibits considerable structural resilience under the applied reaction conditions, accompanied by relatively limited loss of amino-containing functionalities. In contrast, UiO-66@Ala/Br⁻ is particularly susceptible to progressive Br⁻ leaching, which becomes more pronounced during extended recycling and ultimately contributes to the observed decrease in catalytic activity. Nevertheless, the preservation of the primary UiO-66 framework and substantial retention of its chiral environment after repeated catalytic operation highlight the promising structural durability and recyclability of these multifunctional catalysts, while simultaneously identifying anion stabilization as an important avenue for future catalyst development.

Conclusion

In summary, UiO-66 and its L-alanine-functionalized derivative, UiO-66@Ala, were successfully synthesized via a sol–gel method, followed by post-synthetic alkyl-halide functionalization of UiO-66@Ala to incorporate bromide ions, yielding UiO-66@Ala/Br⁻, and the resulting materials were evaluated for the cycloaddition of CO₂ with epoxides. Comprehensive characterization confirmed the successful incorporation of the L-alanine functionality while preserving the crystallinity and structural integrity of the UiO-66 framework. The catalytic results demonstrate that the combination of Zr⁴⁺ Lewis acid sites, -NH functionalities, chiral microenvironments, and Br⁻ nucleophilic sites can synergistically promote epoxide activation, ring opening, and subsequent CO₂ insertion, leading to efficient cyclic carbonate formation with high selectivity. Notably, UiO-66@Ala exhibited excellent catalytic performance in the presence of TBAB, achieving up to 99% conversion of styrene oxide. More importantly, incorporation of Br⁻ into the framework produced UiO-66@Ala/Br⁻, enabling CO₂ cycloaddition without the need for an external co-catalyst. This integrated catalytic design demonstrates the potential of incorporating both catalytic

functionality and nucleophilic species within a single porous framework. Post-catalytic characterization further confirmed the overall structural robustness and retention of the chiral framework, although Br⁻ leaching was observed during repeated cycles and represents an important limitation for further optimization. Overall, this work highlights chiral, cascade functionalization of UiO-66 as a promising platform for selective and more sustainable CO₂ fixation and provides a useful strategy for designing heterogeneous catalysts that minimize reliance on -NH functionalities, external co-catalysts and organic solvents while introducing chiral microenvironments into the structure.

Declarations

ASSOCIATED CONTENT

Supporting Information.

Detailed synthetic procedures, and characterization of MOFs are presented in Supporting Information section. Also, including data such as EDX, FT-IR, N₂ adsorption–desorption, ¹H NMR, TGA/DTG, CD analyses, XPS, along with detailed catalytic experiments and additional CO₂ fixation data.

AUTHOR INFORMATION

Corresponding Author

Ali Morsali, Department of Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran. mail: morsali_a@modares.ac.ir

Author Contributions

Mohammad Mazraeh: Methodology, Investigation, Formal Analysis, Data Curation, Writing – Original Draft, Writing – Review & Editing, Revision, Visualization. **Behnam Habibi:** Formal Analysis, Visualization, Writing – Review & Editing. **Sobhan Rezayati:** Methodology, Writing – Review & Editing. **Ali Morsali:** Conceptualization, Supervision, Project Administration, Resources, Writing – Review & Editing.

Notes

There are no conflicts to declare.

ACKNOWLEDGMENT

This research was supported by Tarbiat Modares University.

Data availability

The data supporting the findings of this study are available from the corresponding author upon formal and reasonable request.

References

1. Tucker M (1995) Carbon dioxide emissions and global GDP. *Ecol Econ* 15(3):215–223. 10.1016/0921-8009(95)00045-3
2. Nordhaus WD (1975) Can we control carbon dioxide? *Am Econ Rev* 109(6):2015–2035. 10.1257/aer.109.6.2015
3. Hassan A, Dar M, Dar MA (2025) Driving CO₂ Conversion to C₁ and C₂ Products on Single-Atom Catalysts: Recent Experimental and Theoretical Insights. *ACS Appl Mater Interfaces* 17(38):53056–53080. 10.1021/acsami.5c11447
4. Zhang G, Yang H, Fei H (2018) Unusual Missing Linkers in an Organosulfonate-Based Primitive-Cubic (pcu)-Type Metal–Organic Framework for CO₂ Capture and Conversion under Ambient Conditions. *ACS Catal* 8(3):2519–2525. 10.1021/acscatal.7b04189
5. Bhanja P, Modak A, Bhaumik A (2018) Supported Porous Nanomaterials as Efficient Heterogeneous Catalysts for CO₂ Fixation Reactions. *Chem Eur J* 24(29):7278–7297. 10.1002/chem.201800075
6. Li Z-J, Sun J-F, Xu Q-Q, Yin J-Z (2021) Homogeneous and Heterogeneous Ionic Liquid System: Promising Ideal Catalysts for the Fixation of CO₂ into Cyclic Carbonates. *ChemCatChem* 13(8):1848–1866. 10.1002/cctc.202001572
7. Dağ AK, Aytar E, Köse A, Ispir E (2026) Schiff base Pd(II) complexes as efficient catalysts for CO₂ conversion to cyclic carbonates under high and atmospheric pressure. *J Organomet Chem* 1047:124028. 10.1016/j.jorganchem.2026.124028
8. Ren Y, Chen J, Qi C, Jiang HA (2015) New Type of Lewis Acid–Base Bifunctional M(salphen) (M = Zn, Cu and Ni) Catalysts for CO₂ Fixation. *ChemCatChem* 7(10):1535–1538. 10.1002/cctc.201500113
9. Dhakshinamoorthy A, Li Z, Garcia H (2018) Catalysis and photocatalysis by metal organic frameworks. *Chem Soc Rev* 47(22):8134–8172. 10.1039/c8cs00256h
10. Corma A, García H, Llabrés i Xamena FX (2010) Engineering Metal Organic Frameworks for Heterogeneous Catalysis. *Chem Rev* 110(8):4606–4655. 10.1021/cr9003924
11. Jiang Z-R, Wang H, Hu Y, Lu J, Jiang H-L (2015) Polar Group and Defect Engineering in a Metal–Organic Framework: Synergistic Promotion of Carbon Dioxide Sorption and Conversion. *ChemSusChem* 8 (5), 878–885. 10.1002/cssc.201403230
12. Kuruppathparambil RR, Jose T, Babu R, Hwang G-Y, Kathalikkattil AC, Kim D-W, Park (2016) D.-W. A room temperature synthesizable and environmental friendly heterogeneous ZIF-67 catalyst for the solvent less and co-catalyst free synthesis of cyclic carbonates. *Appl Catal B: Environ* 182:562–569. 10.1016/j.apcatb.2015.10.005
13. Ugale B, Dhankhar SS, Nagaraja CM (2016) Construction of 3-Fold-Interpenetrated Three-Dimensional Metal–Organic Frameworks of Nickel(II) for Highly Efficient Capture and Conversion of Carbon Dioxide. *Inorg Chem* 55(19):9757–9766. 10.1021/acs.inorgchem.6b01569
14. Mazraeh M, Hedayati Z, Primo A, Dhakshinamoorthy A, Morsali A, Garcia H (2026) Recent advances in multi-metallic organic frameworks and their derivatives for catalysis, electro-/photocatalysis and

- sensing applications. *J Mater Chem A* 14(22):13238–13285. 10.1039/d5ta06669g
15. Wang Z, Hao M, Li C, Gao X, Yu S, Zhao L, Zhang H, Li G, Li Y (2026) Electron-Rich Nanorelay Enhances Ligand-to-Metal Charge Transfer in Lanthanide Metal–Organic Frameworks during Photocatalytic CO₂ Conversion. *Adv Mater* 38(7):e12763. 10.1002/adma.202512763
 16. Sharifinia S, Mazraeh M, Morsali A (2026) The impact of mixed-linker engineering on MOF's electrocatalytic activity. *Coord Chem Rev* 560:217782. 10.1016/j.ccr.2026.217782
 17. Mazraeh M, Dhakshinamoorthy A, Morsali A, Garcia H (2026) Multi-Metallic Organic Framework-Based Composites as Electrocatalysts. *Small* 22(19):e11734. 10.1002/smll.202511734
 18. Li J-R, Sculley J, Zhou H-C (2011) Metal–Organic Frameworks for Separations. *Chem Rev* 112(2):869–932. 10.1021/cr200190s
 19. Moslehabadi RR, Hedayati Z, Mazraeh M, Asghar S, Rouhani F, Morsali A (2025) Sacrificial MOFs on usage: multifunctional compounds. *J Mater Chem B* 13(26):7554–7608. 10.1039/d5tb00764j
 20. Qiongjie D, Yiwei L, Chuncheng S, Jifei X, Wei D, Dong L, Haoyuan C, Baohong L, Jianqiang L (2021) Applications of ROS-Induced Zr-MOFs Platform in Multimodal Synergistic Therapy. *Mini-Reviews Med Chem* 21(13):1718–1733. 10.2174/1389557521666210105111850
 21. Bai Y, Dou Y, Xie L-H, Rutledge W, Li J-R, Zhou H-C (2016) Zr-based metal–organic frameworks: design, synthesis, structure, and applications. *Chem Soc Rev* 45(8):2327–2367. 10.1039/c5cs00837a
 22. Babu R, Kathalikkattil AC, Roshan R, Tharun J, Kim D-W, Park D-W (2016) Dual-porous metal organic framework for room temperature CO₂ fixation via cyclic carbonate synthesis. *Green Chem* 18(1):232–242. 10.1039/c5gc01763g
 23. Abedi S, Azhdari Tehrani A, Ghasempour H, Morsali A (2016) Interplay between hydrophobicity and basicity toward the catalytic activity of isorecticular MOF organocatalysts. *New J Chem* 40(8):6970–6976. 10.1039/c6nj00480f
 24. Taghavi Fardood S, Yekke Zare F, Moradnia F, Ramazani A (2025) Preparation, characterization and photocatalysis performances of superparamagnetic MgFe₂O₄@CeO₂ nanocomposites: Synthesized via an easy and green sol–gel method. *J Rare Earths* 43(4):736–742. 10.1016/j.jre.2024.03.006
 25. Mehta JP, Tian T, Zeng Z, Divitini G, Connolly BM, Midgley PA, Tan J-C, Fairen-Jimenez D, Wheatley AEH (2018) Sol–Gel Synthesis of Robust Metal–Organic Frameworks for Nanoparticle Encapsulation. *Adv Funct Mater* 28(8):1705588. 10.1002/adfm.201705588
 26. Sumida K, Liang K, Reboul J, Ibarra IA, Furukawa S, Falcaro P (2017) Sol–Gel Processing of Metal–Organic Frameworks. *Chem Mater* 29(7):2626–2645. 10.1021/acs.chemmater.6b03934
 27. He H, Perman JA, Zhu G, Ma S (2016) Metal–Organic Frameworks for CO₂ Chemical Transformations. *Small* 12(46):6309–6324. 10.1002/smll.201602711
 28. Rezayati S, Morsali A (2024) Functionalization of Magnetic UiO-66-NH₂ with a Chiral Cu(I–proline)₂ Complex as a Hybrid Asymmetric Catalyst for CO₂ Conversion into Cyclic Carbonates. *Inorg Chem* 63(13):6051–6066. 10.1021/acs.inorgchem.4c00376

29. Connolly BM, Aragonés-Anglada M, Gandara-Loe J, Danaf NA, Lamb DC, Mehta JP, Vulpe D, Wuttke S, Silvestre-Albero J, Moghadam PZ et al (2019) Tuning porosity in macroscopic monolithic metal-organic frameworks for exceptional natural gas storage. *Nat Commun* 10(1):2345. 10.1038/s41467-019-10185-1
30. Tian T, Zeng Z, Vulpe D, Casco ME, Divitini G, Midgley PA, Silvestre-Albero J, Tan J-C, Moghadam PZ, Fairen-Jimenez (2018) D. A sol-gel monolithic metal-organic framework with enhanced methane uptake. *Nat Mater* 17(2):174–179. 10.1038/nmat5050
31. Rayati S, Mazraeh M, Shokoohi S, Nafarieh P, Nejabat F (2024) Synthesis, characterization, and a comparative study on the catalytic activity of the functionalized magnetic nanoparticles for the green oxidation of sulfides. *J Chin Chem Soc* 71(9):1071–1083. 10.1002/jccs.202400119
32. Guo D, Zheng D, Zhou D, Tong C, Huang S (2025) Preparation and application of achiral UiO-66-NH₂ MOFs for enantioselective fluorescent detection of lysine enantiomers. *Talanta* 282:126972. 10.1016/j.talanta.2024.126972
33. Xu J, Zhang Y, Liu S, Ma Q, Liu Z, Guo Z, Huang X (2025) Host-guest recognition-enabled ion current rectification in amino acid-decorated UiO-66 nanochannels for Co²⁺ analysis. *Chem Eng J* 523:168429. 10.1016/j.cej.2025.168429
34. Wang R, Liu L, Subhan S, Muhammad Y, Hu Y, Huang M, Peng Y, Zhao Z, Zhao Z (2020) Engineering pH-switchable UiO-66 via in-situ amino acid doping for highly selective adsorption of anionic dyes. *Chem Eng J* 395:124958. 10.1016/j.cej.2020.124958
35. Shearer GC, Chavan S, Bordiga S, Svelle S, Olsbye U, Lillerud KP (2016) Defect Engineering: Tuning the Porosity and Composition of the Metal-Organic Framework UiO-66 via Modulated Synthesis. *Chem Mater* 28(11):3749–3761. 10.1021/acs.chemmater.6b00602
36. Shearer GC, Vitillo JG, Bordiga S, Svelle S, Olsbye U, Lillerud KP (2016) Functionalizing the defects: postsynthetic ligand exchange in the metal organic framework UiO-66. *Chem Mater* 28(20):7190–7193. 10.1021/acs.chemmater.6b02749
37. Cao J, Xu Z, Chen Y, Li S, Jiang Y, Bai L, Yu H, Li H, Bian Z (2023) Tailoring the Asymmetric Structure of NH₂-UiO-66 Metal-Organic Frameworks for Light-promoted Selective and Efficient Gold Extraction and Separation. *Angew Chem* 135(18):e202302202. 10.1002/ange.202302202
38. Rezayati S, Liu R, Zhang G, Morsali A, Ramazani A (2026) Chiral magnetic catalysts: Immobilization of copper(II) and nickel(II) salen complexes on UiO-66-NH₂ composites for enhanced asymmetric catalysis. *Appl Mater Today* 49:103126. 10.1016/j.apmt.2026.103126
39. Razavi SAA, Sharifzadeh Z, Morsali A (2024) Functionalization of Defective Zr Metal-Organic Frameworks for Water Decontamination: Mechanistic Insight into the Competitive Roles of -NH₂ and -SH Sites in Removal of As(III) Species. *Inorg Chem* 63(11):5107–5119. 10.1021/acs.inorgchem.3c04640
40. Liu J, Wang X, Zhao Y, Xu Y, Pan Y, Feng S, Liu J, Huang X, Wang H (2022) NH₃ Plasma Functionalization of UiO-66-NH₂ for Highly Enhanced Selective Fluorescence Detection of U(VI) in

Figures

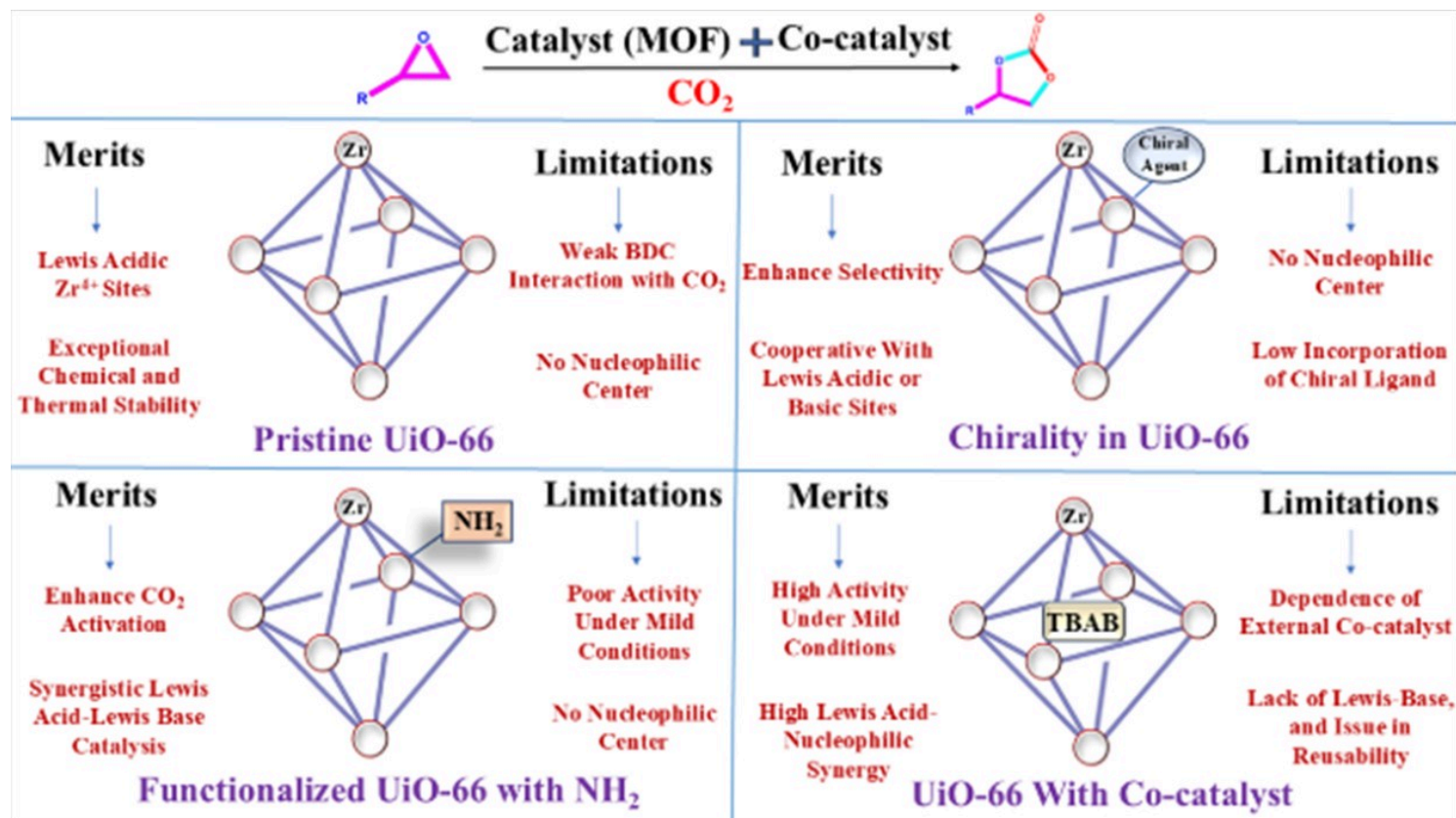


Figure 1

Merits and limitations of individual modification on UiO-66 in catalytic CO_2 fixation.

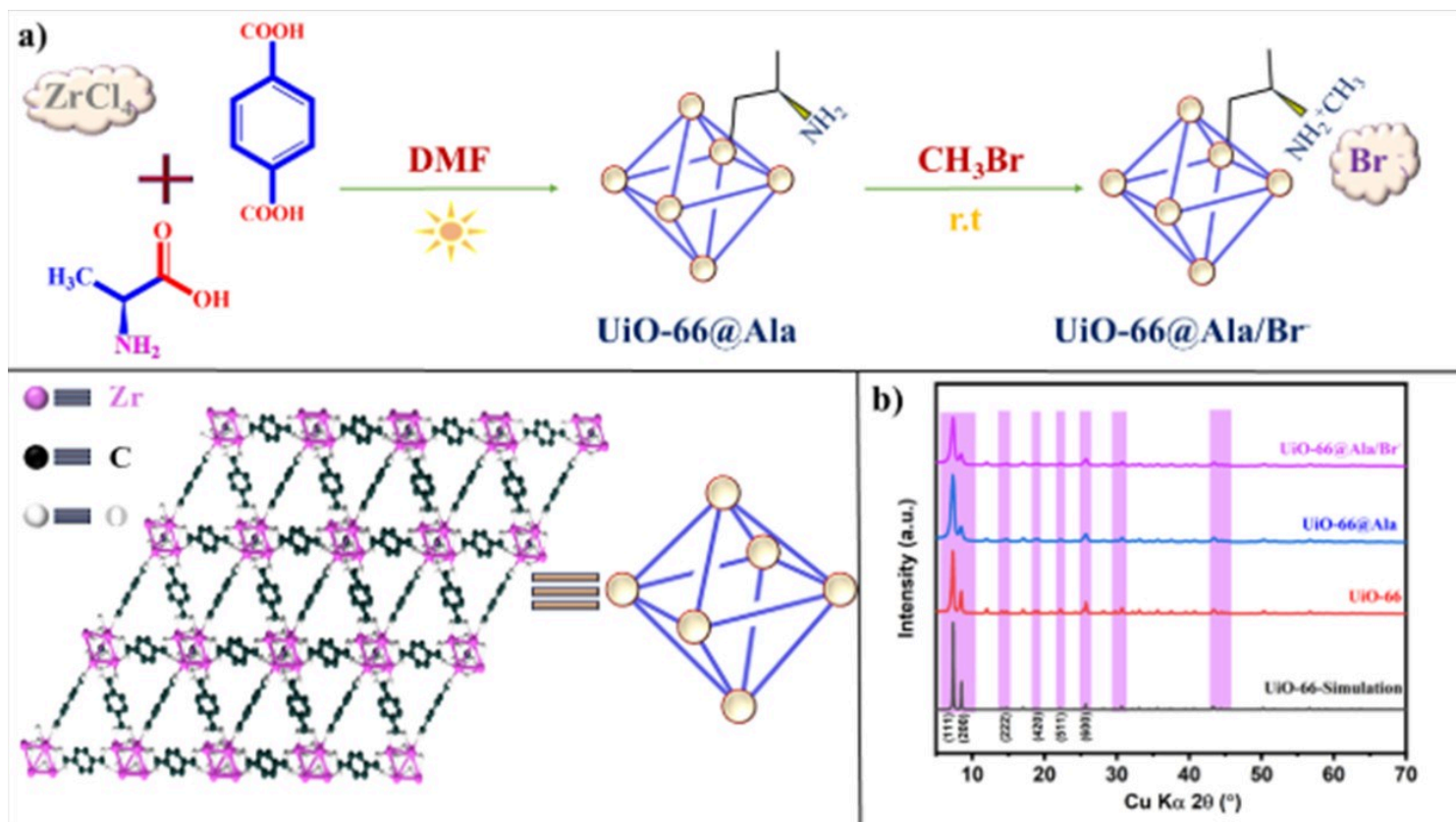


Figure 2

a) Schematic illustration of the general synthesis strategy and proposed structural architectures of UiO-66@Ala and UiO-66@Ala/Br⁻, and b) PXRD patterns of the as-synthesized UiO-66, UiO-66@Ala, and UiO-66@Ala/Br⁻, together with their corresponding simulated patterns for structural comparison.

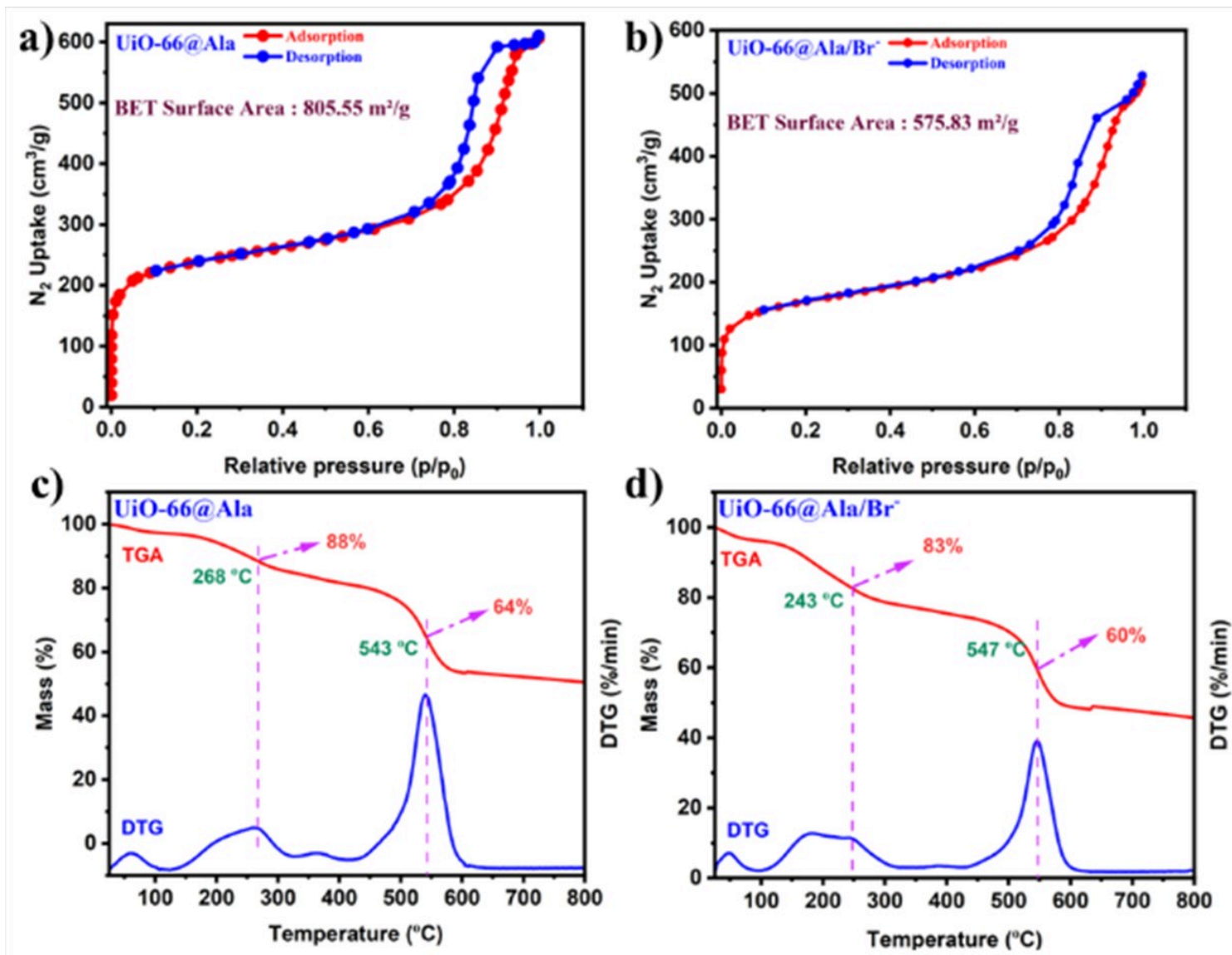


Figure 3

N₂ adsorption-desorption isotherms and corresponding BET surface-area analyses of a) UiO-66@Ala and b) UiO-66@Ala/Br⁻; and TGA/DTG profiles of c) UiO-66@Ala and d) UiO-66@Ala/Br⁻.

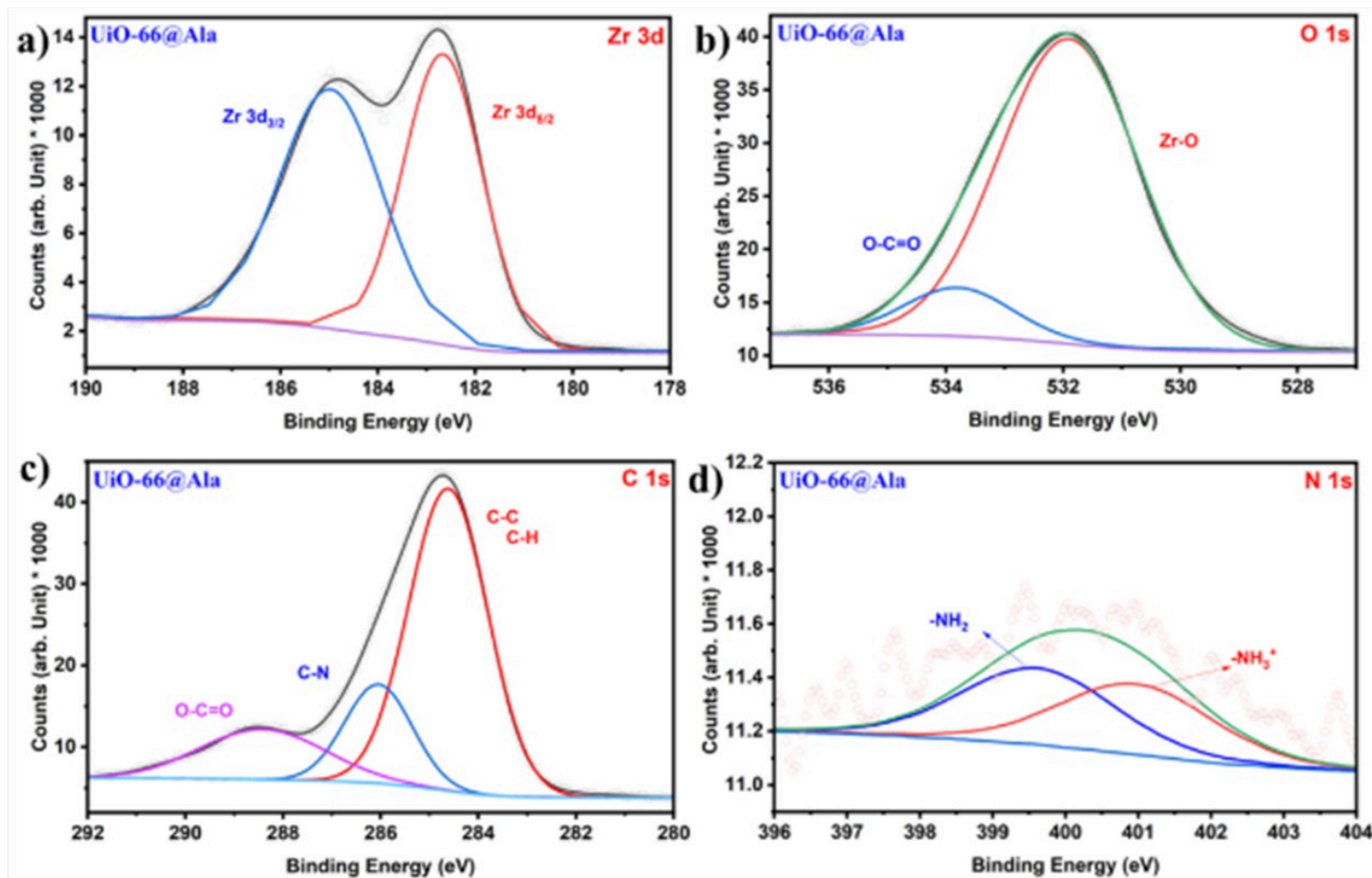


Figure 4

XPS spectra of UiO-66@Ala: a) Zr 3d, b) O 1s, c) C 1s, and d) N 1s.

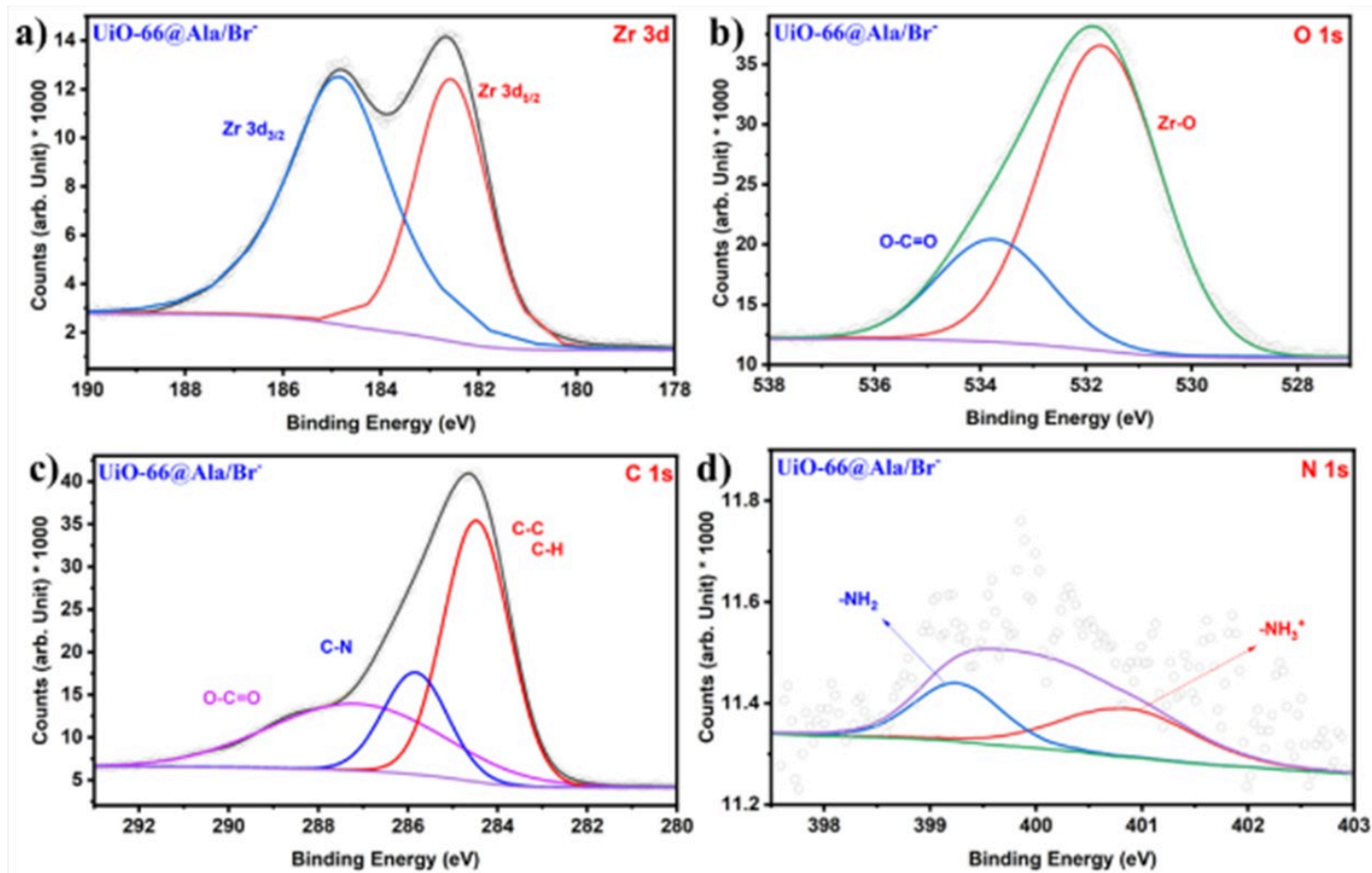


Figure 5

XPS spectra of UiO-66@Ala/Br⁻: a) Zr 3d, b) O 1s, c) C 1s, and d) N 1s.

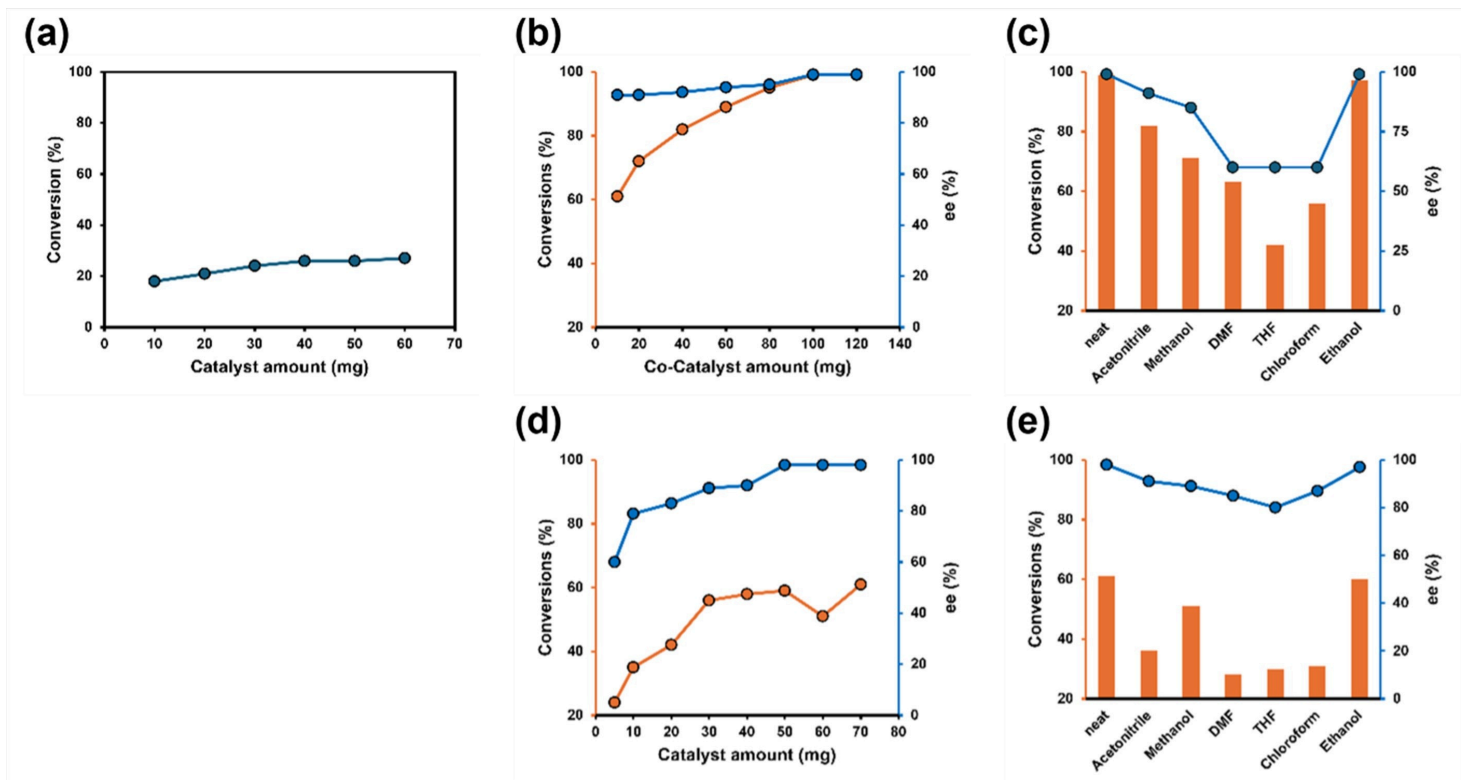


Figure 6

Optimization of the CO₂ cycloaddition reaction using (a-c) UiO-66@Ala and (d-e) UiO-66@Ala/Br⁻. (a, d) effect of catalyst loading, (b) effect of TBAB loading, (c, e) effect of solvent on epoxide conversion and enantiomer excess; Reaction conditions: UiO-66@Ala: 12 h, 80 °C; 30 mg catalyst was used for panels (b,c), and 100 mg TBAB was used for panel (c); solvent-containing reactions were conducted under reflux. UiO-66@Ala/Br⁻: 24 h, 80 °C, without external co-catalyst; solvent-containing reactions were conducted under reflux.

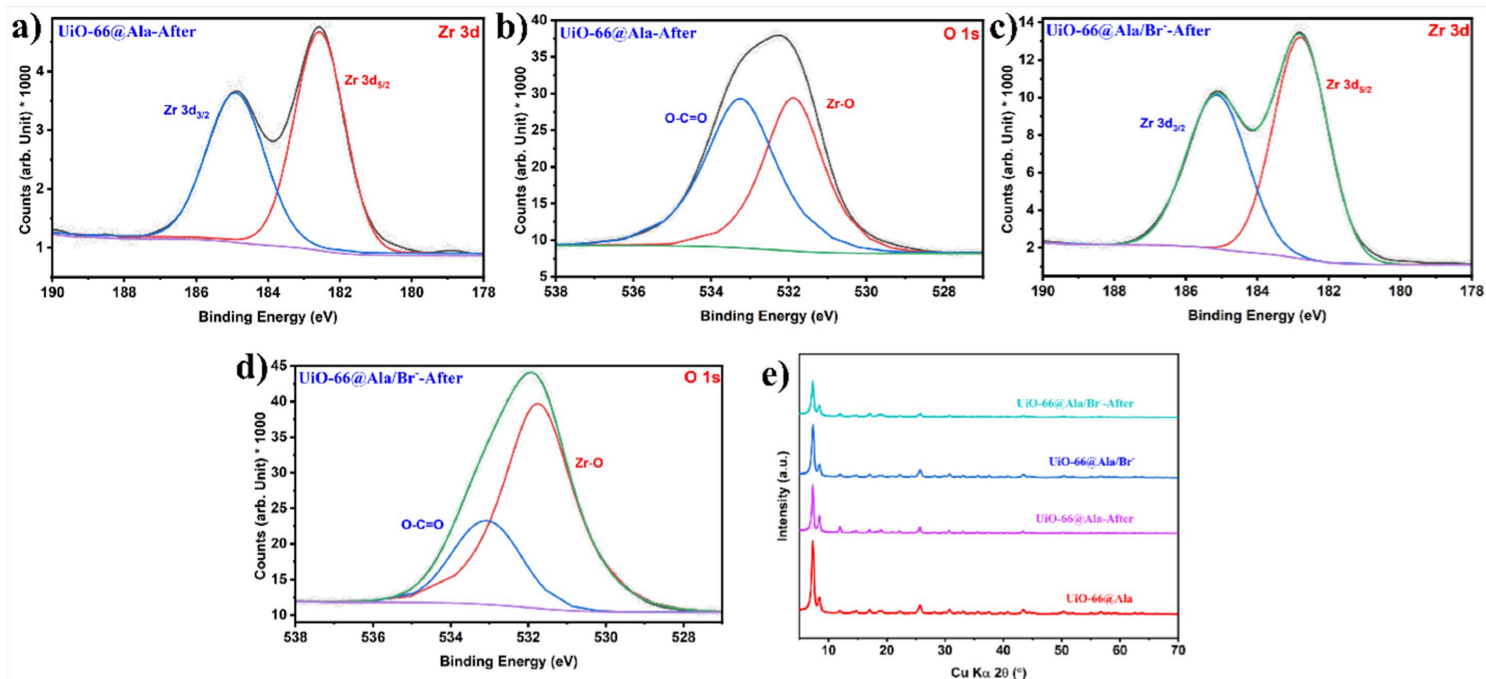


Figure 7

Post-catalytic characterization of UiO-66@Ala and UiO-66@Ala/Br⁻ after five cycles of CO₂ fixation: XPS spectra of a) Zr 3d and b) O 1s for UiO-66@Ala; XPS spectra of c) Zr 3d and d) O 1s for UiO-66@Ala/Br⁻; and e) comparison of the PXRD patterns of UiO-66@Ala and UiO-66@Ala/Br⁻ before and after five catalytic cycles.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.docx](#)
- [TOC.docx](#)