

MoO₂(acac)₂-encapsulated in TS-1 zeolite catalyst for CO₂ coupling with olefins to cyclic carbonates

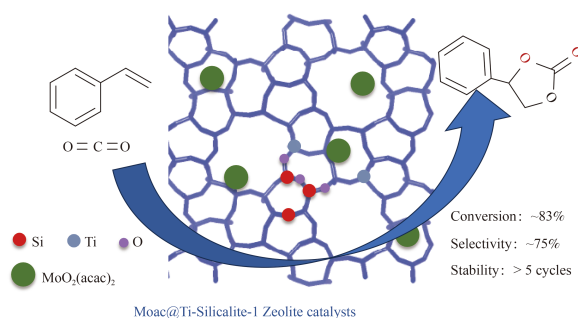
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Abstract: The coupling of CO₂ with olefins to produce cyclic carbonates has emerged as an important research topic in sustainable chemistry, owing to its high atom economy and the wide applicability of the resulting products. However, this reaction faces a significant challenge due to the mismatch between the rates of the epoxidation and cycloaddition steps. In this work, a series of TS-1 zeolite catalysts encapsulating different amounts of molybdenum acetylacetonate were prepared through hydrothermal synthesis followed by post-treatment, with the aim of elucidating the rate balance between the epoxidation and cycloaddition steps and the underlying regulation mechanism. Characterization results show that the Mo species were present as highly dispersed molybdenum acetylacetonate complexes that were stably confined within the TS-1 framework. These complexes interact electronically with the tetra-coordinated Ti sites to form synergistic active centers, while imposing negligible effects on the zeolite structure and porosity. In the CO₂-styrene coupling reaction, tuning the Mo loading enabled effective control over the epoxidation rate, thereby achieving an appropriate balance with the subsequent cycloaddition step. The optimized catalyst delivered excellent performance under mild conditions, with a styrene conversion of 83.4% and a selectivity of 75.3%, and also exhibited outstanding recyclability. Overall, this encapsulated catalyst successfully addresses the dual challenges of rate matching and active-site stability in CO₂-olefin coupling, providing valuable insights for the rational design of efficient, durable bifunctional catalysts.

Key words: TS-1 zeolite; molybdenyl acetylacetonate; encapsulation; CO₂ conversion; cyclic carbonates



Carbon dioxide (CO₂) is not only one of the major greenhouse gases but also an inexpensive, non-toxic, non-flammable, and abundant C1 feedstock^[1] and its catalytic conversion has attracted widespread attention in recent years^[2–3]. Significant advances have been made in the synthesis of renewable fuels and chemicals—such as methanol^[4–5], aromatics^[6–7] and olefins^[8–9]—through CO₂ hydrogenation. Meanwhile, CO₂ can selectively couple with epoxides to form cyclic carbonates with high selectivity^[10–11], which are essential chemical intermediates widely used in biodegradable materials, polar aprotic

solvents, and polymer synthesis^[12]. Despite the advantages of high atom economy and industrial scalability, the use of epoxides as starting materials presents safety and environmental concerns due to their toxicity and high reactivity^[13–14]. Compared with epoxides, olefins are more accessible, less toxic and cheaper, making them attractive and sustainable alternatives. Therefore, the direct one-step one-pot conversion of olefins and CO₂ into cyclic carbonates has emerged as a promising strategy^[15]. The transformation requires the catalyst to efficiently mediate two consecutive steps—olefin epoxidation and CO₂

Received: 2025-10-11; Revised: 2025-10-29

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Foundation items: Supported by Guangdong Basic and Applied Basic Research Foundation (2023A1515012115) and the National Natural Science Foundation of China (22072174).

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DOI: 10.1016/S1872-5813(25)60628-1 CSTR: 32157.14.2097-213X.2025.JFCT.0181 Associated Data DOI: 10.57760/sciencedb.j00124.00290

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cycloaddition. Integrating these steps not only eliminates the need to handle reactive epoxide intermediates but also simplifies the overall process, offering advantages in both environmental compatibility and economic performance^[16–17].

Achieving a balanced match between the epoxidation and CO_2 cycloaddition steps through precise catalyst design is the key challenge for one-pot olefin- CO_2 conversion to cyclic carbonates. Earlier studies mainly focused on homogeneous catalysts, which typically exhibit excellent activity but suffer from difficult separation and poor recyclability, thus limiting their practical application. Consequently, research has gradually shifted toward heterogeneous systems, including metal oxides, zeolites, MOFs and supported composite catalysts. For example, Aresta et al.^[18] employed various metal oxides for the reaction of styrene with CO_2 to synthesize styrene carbonate, and found Nb_2O_5 showed the best performance, achieving a 27% styrene conversion and nearly a 17% carbonate yield under conditions of 4.5 MPa CO_2 and 110 °C. Zalomaeva et al.^[19] developed a Cr-MIL-101 catalyst that enabled the oxidative carboxylation of styrene to synthesize the cyclic carbonate. Although the reaction conditions were mild, the styrene conversion was 17% with a cyclic carbonate selectivity of only 25%, and significant amounts of benzaldehyde (69% selectivity) were generated as a by-product. Huang et al.^[20] developed transition metal (Zn^{2+} , Mn^{2+} , Cr^{2+} , Co^{2+} , Fe^{3+} , etc.) doped g- C_3N_4 composite catalysts with SBA-15. Among them, Fe-g- C_3N_4 /SBA-15 showed the best catalytic effect, yielding styrene carbonate with a 32% yield. These studies collectively highlight that achieving high conversion and selectivity in heterogeneous systems requires a rational balance between epoxidation and cycloaddition functions, as well as sufficient catalyst stability under liquid-phase, high-temperature, and high-pressure CO_2 conditions.

Molybdenum acetylacetonate ($\text{MoO}_2(\text{acac})_2$) is a homogeneous catalyst widely applied in the olefin epoxidation. For example, research conducted by Fusi et al.^[21] and Farias et al.^[22] has demonstrated that $\text{MoO}_2(\text{acac})_2$ exhibits superior catalytic performance in epoxidation processes, effectively catalyzing the epoxidation of complex substrates such as cyclohexene and soybean oil (achieving a maximum conversion of 94.1%). However, the high recovery costs and limited reusability associated with its homogeneous nature significantly restrict its broader application. Meanwhile, titanium silicalite-1 (TS-1) is preferred in the field of olefin epoxidation owing to its isolated tetrahedral Ti active sites within the framework, combined with high hydrothermal stability and the advantage of facile separation. Research conducted by Shen et al.^[23] and Ma et al.^[24] confirms the capability of TS-1 for high conversion and selectivity in the epoxidation of propylene and butene. Nevertheless, in the tandem reaction involving the direct synthesis of cyclic carbonates from olefins and CO_2 , the catalytic efficiency of the TS-1 zeolite catalyst remains suboptimal; its autonomous catalytic capability is insufficient to effectively regulate the entire

tandem process.

Considering the widespread application of TS-1 zeolite in olefin epoxidation^[25] and the efficient activation performance of molybdenum acetylacetonate towards oxidants under mild conditions^[26], we designed a bifunctional catalyst in which $\text{MoO}_2(\text{acac})_2$ species were encapsulated within the TS-1 framework through a combined hydrothermal and post-treatment route. This approach allows the Mo complexes to be stably confined in the zeolite channels while preserving the integrity of the TS-1 framework. The encapsulated Mo species cooperate electronically with the tetrahedral Ti sites to enhance olefin epoxidation activity, and the confined structure ensures excellent long-term stability. By systematically adjusting the content of molybdenum acetylacetonate, we successfully balanced the epoxidation and CO_2 cycloaddition reaction. The preferred catalyst achieved a styrene conversion of 83.4% with a target product selectivity of 75.3%, along with excellent cycling stability. This study, therefore, provides an effective strategy for addressing the rate-matching challenge in tandem olefin- CO_2 conversions.

1 Experimental

1.1 Catalyst preparation

1.1.1 Chemicals and reactants

All chemical reagents used in this experiment were of analytical grade and used without further purification. Tetraethyl orthosilicate (TEOS, $\text{SiO}_2 \geq 28\%$), tetrabutyl titanate (TBOT, 98%) and styrene (99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tetrapropylammonium hydroxide (TPAOH, 25% in water), tetrabutylammonium bromide (TBAB, 98%), acetylacetone (99%), and ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 99%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Tert-butyl hydroperoxide (TBHP, 25% aqueous solution) was purchased from Shanghai Meryer Biochemical Technology Co., Ltd. Nitric acid (65%) and ammonia solution (25%–28% aqueous solution) were purchased from Xilong Scientific Co., Ltd.

1.1.2 Preparation of Mo encapsulated in TS-1 zeolite (Mo@TS)

The Mo@TS zeolite was synthesized *via* a hydrothermal route^[27]. TEOS, TBOT, ammonium molybdate tetrahydrate, and TPAOH were used as the silicon source, titanium source, molybdenum source, and organic structure-directing agent, respectively, for the preparation of the TS-1 zeolite. Typically, a certain amount of TEOS and TBOT was first mixed and stirred continuously at room temperature for 1 h. Subsequently, an aqueous solution of ammonium molybdate

was slowly added dropwise under vigorous stirring and aged for 0.5 h. Then, the resulting mixture was slowly added dropwise into an aqueous TPAOH solution to form a homogeneous gel. After aging at 60 °C for 3 h, the gel was transferred to a Teflon-lined autoclave and crystallized at 175 °C for 24 h under rotation (20 r/min). The molar composition of the initial gel was $\text{SiO}_2\cdot\text{TiO}_2\cdot\text{TPAOH}\cdot\text{H}_2\text{O}:\text{MoO}_3 = 1.0:0.04:0.50:33:X$, where X represents the molar amount of MoO_3 used. The Mo loading ratio was calculated based on the total amount of SiO_2 and TiO_2 in the initial gel. By adjusting X (1.05×10^{-4} , 1.32×10^{-4} , 1.59×10^{-4} and 1.86×10^{-4}), Mo@TS samples with different Mo loadings were obtained. Following crystallization, the solids were filtered, washed to neutral pH value, dried at 80 °C overnight, and calcined at 550 °C for 8 h. A series of Mo@TS zeolites with different encapsulation contents was ultimately obtained, designated as $x\text{Mo@TS}$ (where $x = 1.5, 2.5, 3$ and 3.5 , representing the Mo loading in weight percentage). For comparison, a TS-1 zeolite was also synthesized without adding the Mo precursor, following the same preparation and calcination procedures as the $x\text{Mo@TS}$ samples.

1.1.3 Preparation of $\text{MoO}_2(\text{acac})_2$ encapsulated in TS-1 catalyst (Moac@TS)

The as-prepared $x\text{Mo@TS}$ zeolite (where $x = 1.5, 2.5, 3$ and 3.5) was dispersed in a 1.0% ammonia solution and stirred at room temperature for 5 min to form a homogeneous suspension. Acetylacetone (acac) was then added dropwise and stirred for an additional 20 min to ensure coordination with the encapsulated Mo species. The pH was adjusted to neutral by adding 0.5% HNO_3 . After cooling, the solids were collected by high-speed centrifugation and washed thoroughly with deionized water and ethanol. The final products were dried at 120 °C to obtain the encapsulated structured Moac@TS catalysts, designated as $x\text{Moac@TS}$.

1.2 Characterizations

XRD patterns were recorded on a Rigaku diffractometer (Smart Lab) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA, respectively. Data were collected from 5° to 50° (2θ), with a step size of 0.02° and a scan rate of 2°/min.

Fourier-transform infrared (FT-IR) spectroscopy was conducted in transmission mode utilizing a Thermo iS5 instrument to identify the functional groups associated with the Mo species.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F3 Tarsus thermogravimetric analyzer. The samples were heated from 50 to 800 °C under a N_2 atmosphere at a heating rate of 10 °C/min.

The molybdenum content in representative samples was determined using an Agilent 5110 inductively coupled

plasma optical emission spectrometer (ICP-OES).

Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis, Lambda 950) was used to detect the coordination environment and chemical state of Mo species in the samples, with BaSO_4 employed as the internal reflectance standard.

A Talos F200X transmission electron microscope (TEM) operating at 200 kV was utilized to obtain the morphology and crystal size of the samples. The samples were ground and dispersed in ethanol, and then dropped onto Cu grids with an ultra-thin carbon film. Element distributions were obtained in the scanning transmission electron microscopy (STEM) mode, using a high-angle annular dark-field (HAADF) detector with a frame time of 20 seconds.

N_2 adsorption-desorption measurements were conducted on a Micromeritics ASAP 2460 analyzer. Samples were degassed at 150 °C for 8 h to remove adsorbed water and impurities before testing. The Brunauer-Emmett-Teller (BET) method was used to calculate specific surface areas, the t -plot method for micropore volumes, and the total pore volume was estimated at $p/p_0 = 0.95$.

X-ray photoelectron spectra (XPS) were conducted on a ThermoFisher ESCALAB 250Xi spectrometer equipped with an $\text{Al K}\alpha$ (1486.7 eV) quartz monochromator source to analyze the surface elemental composition and electronic states of the catalysts. Spectra were fitted with Gaussian-Lorentzian functions following Shirley or Tougaard background subtraction.

1.3 Catalytic evaluations

The catalytic performance was evaluated in a solvent-free system using a stainless steel autoclave reactor. Typically, 9.6 mmol of styrene, 14.4 mmol of TBHP, 0.96 mmol of TBAB and 200 mg of the catalyst were added to the reactor. The reactor was purged three times with high-purity N_2 and then three purges with high-purity CO_2 before being pressurized to 1.0 MPa with CO_2 . Under stirring, the reactor was heated to 70 °C at a heating rate of 1 °C/min and maintained at this temperature for 24 h. After the reaction, the autoclave was cooled to room temperature, and the residual CO_2 was then released slowly. The catalyst was separated by centrifugation and washed three times with dichloromethane to dissolve and remove adsorbed reactants and products. The collected organic phases were combined and concentrated using a rotary evaporator. Product analysis was performed using an Agilent 8860 gas chromatograph equipped with a flame ionization detector (FID) and an HP-INNOWax capillary column (60 m $\times$ 0.320 mm $\times$ 0.25 μm). Dodecane was used as an internal standard for quantifying conversion and selectivity.

The styrene conversion (x) and styrene carbonate selectivity (s) were calculated as follows:

$$x(\%) = \frac{n_{s0} - n_{s1}}{n_{s0}} \times 100\% \quad (1)$$

where the n_{s0} and n_{s1} are the moles of styrene before and

after the reaction, respectively.

$$s(\%) = \frac{n_{\text{sc}}}{n_{\text{s0}} - n_{\text{s1}}} \times 100\% \quad (2)$$

where the n_{sc} is the mole of styrene carbonate in the product after the reaction.

2 Results and discussion

2.1 Physicochemical properties of the encapsulated catalysts

The TS-1 zeolite and the series of Moac@TS catalysts were analyzed by ICP-OES, and the results are summarized in Table 1. The Si/Ti molar ratio of the synthesized TS-1 zeolite was 28.9, slightly lower than the initial gel ratio, indicating incomplete incorporation of Si species into the zeolite framework during crystallization. The Mo contents of the Moac@TS catalysts were also lower than the nominal loadings, which may be attributed to incomplete incorporation of molybdenum species during the crystallization stage and the dissolution of a small fraction of MoO_3 during the *in situ* formation of the molybdenum acetylacetonate complex.

Figure 1(a) shows the XRD patterns of the TS-1 and the Mo-containing samples. The TS-1 zeolite exhibits sharp diffraction peaks at $2\theta = 7.8^\circ, 8.8^\circ, 23.0^\circ, 23.4^\circ$ and 24.4° , confirming the formation of the MFI framework^[28]. The

Mo@TS samples exhibit a similar set of reflections without additional peaks corresponding to Mo oxides or amorphous impurities, demonstrating that the introduction of a small amount of Mo precursor does not disrupt the crystallization of TS-1 or alter its framework order. Likewise, the Moac@TS samples retain the well-defined MFI diffraction pattern. The absence of any Mo-related reflections confirms that the encapsulated molybdenum acetylacetonate species are highly dispersed and/or present at concentrations below the XRD detection threshold. These XRD results collectively indicate that the crystallinity of TS-1 remains intact throughout both the Mo incorporation stage and the subsequent ligand-exchange process.

Figure 1(b) presents the N_2 adsorption-desorption isotherms of the pristine TS-1 zeolite and the $x\text{Moac@TS}$ catalyst series. The textural parameters of the samples are listed in Table 1. TS-1 zeolite exhibits a mixed type I/IV isotherm with a clear hysteresis loop observed near $p/p_0 \approx 0.9$, reflecting its microporous channels and intercrystalline mesoporosity formed by the stacking of crystals. Upon Mo incorporation during crystallization, the resulting Mo@TS sample shows a slight decrease in the micropore surface area and pore volume, suggesting that a proportion of Mo species is embedded within or partially blocks the micropores. For the $x\text{Moac@TS}$ catalysts with varying Mo loadings, a gradual decrease in the micropore surface area is observed as the Moac content increases, while the external surface area exhibits a slight increase.

Table 1 Textural properties of the TS-1 zeolite and Moac@TS series catalysts

Sample	Surface area/($\text{m}^2 \cdot \text{g}^{-1}$)		Pore volume/($\text{cm}^3 \cdot \text{g}^{-1}$)		Mo content w/%	Weight w/%	Relative crystallinity ^b
	S_{mic}	S_{ex}	V_{t}	V_{mic}			
TS-1	288.3	175.9	0.24	0.104	—	—	1.00
3Mo@TS	250.6	178.1	0.25	0.085	—	—	0.97
1.5Moac@TS	245.7	182.4	0.26	0.083	1.27	3.6 ^a	0.98
2.5Moac@TS	239.2	180.6	0.25	0.083	2.04	4.9	0.98
3Moac@TS	232.7	192.2	0.24	0.085	2.80	6.8	0.97
3.5Moac@TS	229.9	191.8	0.25	0.092	3.26	7.8	0.97

^a: Water adsorption in each catalyst within 50–150 °C was deducted; ^b: Crystallinity was defined relative to that of the TS-1 zeolite, which was set to 1.0.

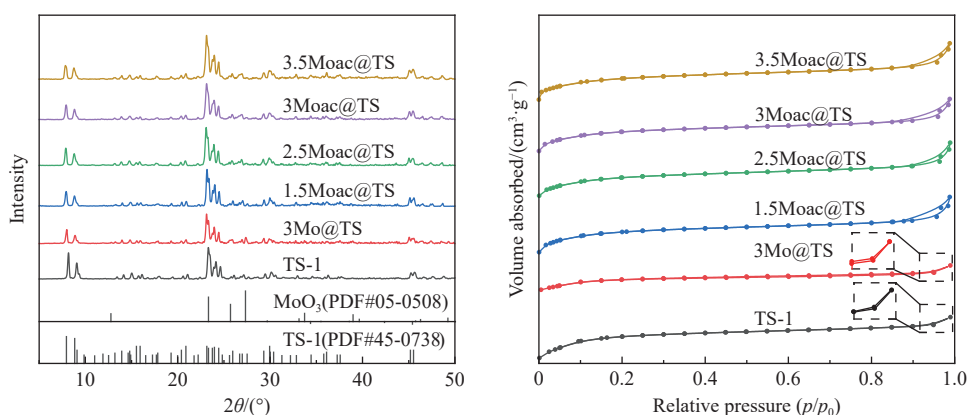


Fig. 1 XRD patterns (a) and N_2 -physisorption spectra (b) of TS-1 zeolite and Moac@TS series catalysts

This result indicates that the encapsulated Moac complexes occupy part of zeolite micropores and that the mild *in situ* synthesis route may cause subtle modifications of the crystal surface or defects, thereby increasing the external surface area contribution. Importantly, all catalysts exhibit no significant difference in micropore volume relative to pristine TS-1, implying that the microporous framework remains largely undisturbed. Combined with the XRD, these results confirm that the Moac complexes exist in a highly dispersed state within the TS-1 zeolite structure rather than forming large aggregates.

FT-IR spectra of TS-1 and $x\text{Moac@TS}$ catalysts are shown in Figure 2(a). All samples exhibit characteristic vibration bands at 450, 800 and 1100 cm^{-1} , attributed to the bending vibration of the Ti–O–Si bond and the symmetric and asymmetric stretching vibrations of Si–O–Si bonds in the TS-1 zeolite framework, respectively. Bands at 547 and 1230 cm^{-1} correspond to the framework vibrations of the MFI topology, which are also preserved, indicating that TS-1 framework remains intact after Mo encapsulation. The Moac@TS catalysts show additional characteristic bands at 1360 and 1589 cm^{-1} , corresponding to the C=C stretching vibrations of the acetylacetonate ligand, and a band at 905 cm^{-1} attributable to the Mo=O stretching vibration in the MoO_2 unit of molybdenum acetylacetonate^[29]. The retention of MFI-related framework peaks alongside the emergence of ligand-associated peaks provides direct evidence that molybdenum acetylacetonate species have been successfully encapsulated within the zeolite without disrupting the TS-1 structure.

Figure 2(b) displays the UV-vis spectra of the samples. TS-1 and Mo@TS show strong absorption peak at 200–300 nm, assigned to tetrahedrally coordinated Ti species within the zeolite framework. The absence of characteristic absorption peaks near 260 or 330 nm confirms that neither extra-framework octahedral Ti species nor anatase TiO_2 is present. In the UV-vis spectra of the $x\text{Moac@TS}$ catalysts, in addition to the characteristic peak of the tetrahedrally coordinated Ti species, a broad absorption band is observed near 300 nm, which originates from the $\pi \rightarrow \pi^*$ electron transition in the acetylacetonate (acac) group. Meanwhile, an additional absorption peak observed at 360 nm is

assigned to the ligand-to-metal charge transfer (LMCT) from the acetylacetonate ligand to the Mo center. These features unambiguously confirm that the Mo species in the Moac@TS catalysts primarily exist as molybdenum acetylacetonate complexes with the zeolite channels^[30]. This is fully consistent with the FT-IR results.

Figure 3 shows TEM images and elemental mappings of TS-1 and 3Moac@TS. The pristine sample displays typical coffin-shaped crystal morphology^[31]. After encapsulation, the Moac@TS sample maintains the same morphology with no observable nanoparticles or clusters, indicating that the Moac complex is highly dispersed within the zeolite. Furthermore, STEM-HAADF and EDS elemental mapping reveal uniform distribution of Si, Ti and Mo throughout the zeolite crystals, providing direct evidence that the Moac species are incorporated within the crystalline domain rather than forming external aggregates. In summary, these microscopic observations visually demonstrate that the preparation strategy in this study not only effectively confines the Mo species within the zeolite structure but also ensures their high dispersion, thereby laying the structural foundation for the subsequent catalytic performance.

To systematically evaluate the molybdenum acetylacetonate content and thermal stability, TGA was performed on the pristine TS-1 zeolite and the catalyst samples, as shown in Figure 4. TS-1 zeolite exhibits only a single weight-loss event below 150 °C, which is primarily attributed to the removal of water adsorbed on the zeolite surface and within its pores. The Moac@TS catalysts display continuous weight loss from 50 to 700 °C. The low-temperature loss (<150 °C) decreases as Moac loading increases, reflecting the introduction of Mo species during synthesis and the subsequent *in situ* conversion to molybdenum acetylacetonate alters the inherent hydrophobicity of TS-1, for instance, potentially generating a small number of hydrophilic Si–OH groups. The weight loss in the medium-to-high temperature region (150–600 °C) originates from the decomposition and combustion of the organic acetylacetonate ligands, and the magnitude of this loss correlates with the Mo content measured by ICP-OES (Table 1).

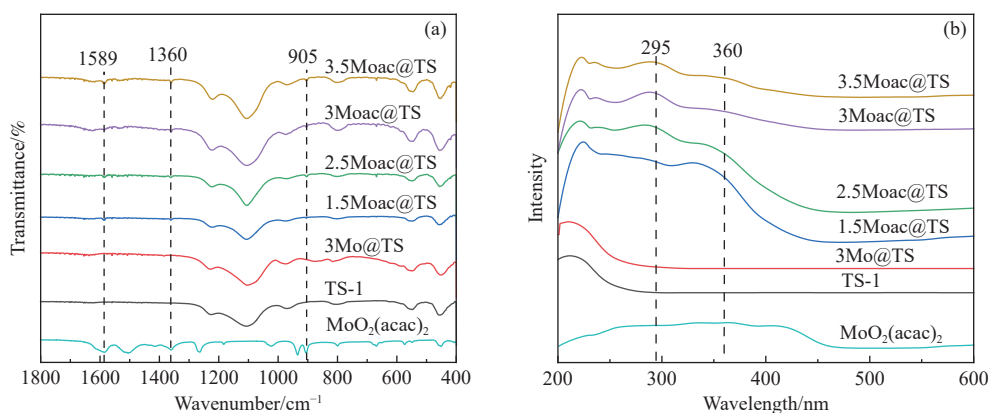


Fig. 2 FT-IR (a) and UV-vis spectra (b) of TS-1 zeolite and Moac@TS series catalysts

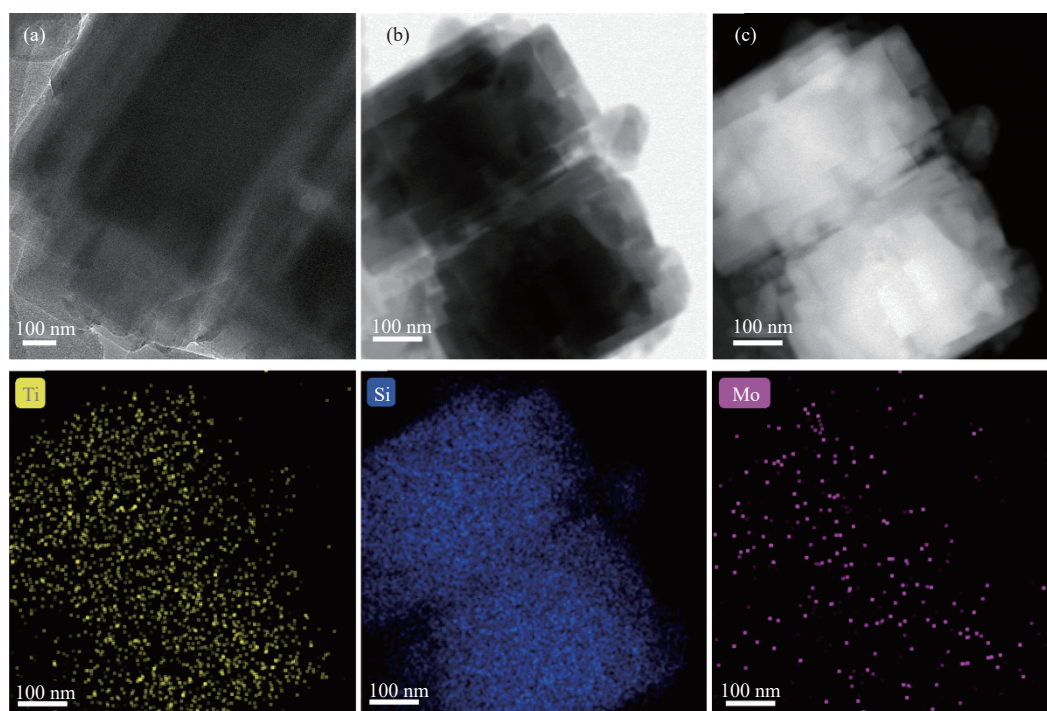


Fig. 3 TEM images of TS-1 (a), 3Moac@TS zeolite catalyst (b) and their corresponding high-angle annular dark-field (HAADF) image (c), along with the respective EDS elemental maps

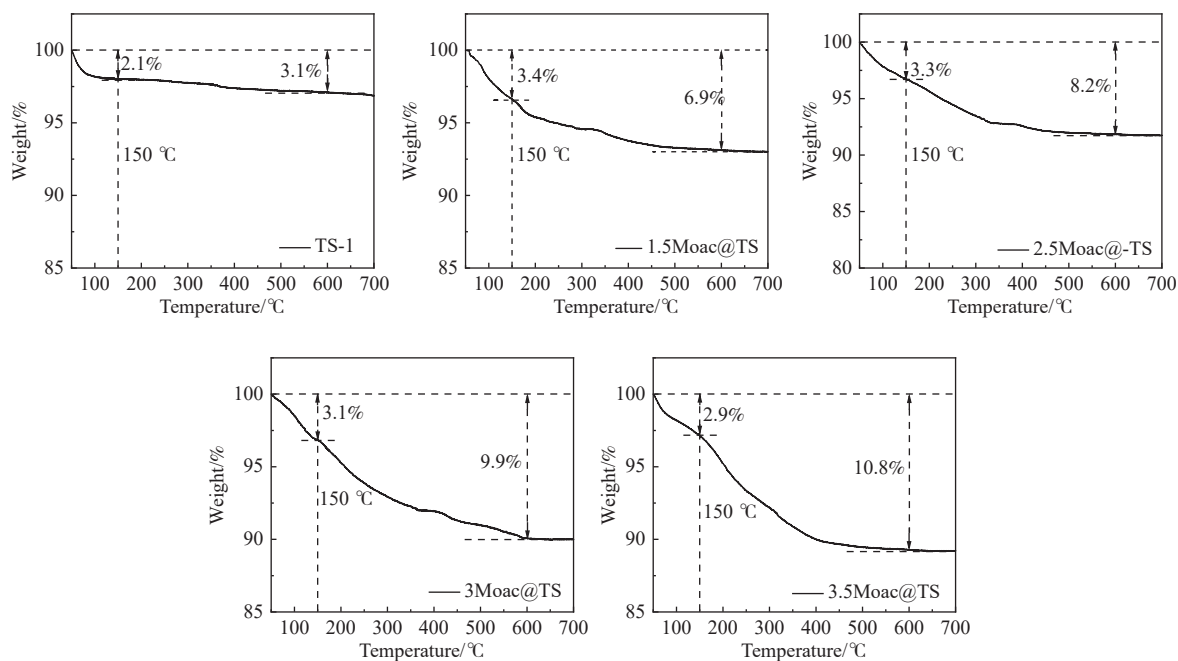


Fig. 4 TGA profiles of TS-1 zeolite and the Moac@TS series catalysts

This correlation confirms the successful encapsulation of Mo species in the form of molybdenum acetylacetonate within the TS-1 zeolite structure. These results indicate that the introduced Mo species influence the zeolite framework structure and surface micro-environment, promoting interactions with the zeolite and leading to the formation of a stable encapsulated structure. The Mo species are stably incorporated within the TS-1 zeolite framework as the relatively hydrophobic Moac, in accordance with the FT-IR and UV-vis analyses. Importantly, the decomposition

temperature of the ligand exceeds the catalytic reaction temperature of (70 °C), demonstrating that the Moac complexes remain structurally stable under catalytic conditions.

XPS was employed to analyze the electronic environments of Ti and Mo in the Moac@TS-1 catalysts. As shown in Figure 5(b), TS-1 zeolite exhibits Ti $2p_{1/2}$ and Ti $2p_{3/2}$ peaks at 460.0 and 465.5 eV, respectively, indicating that Ti exists in a tetrahedral coordination within the zeolite framework. In Moac@TS catalysts, the Ti $2p$ peaks shift

slightly to lower binding energy (459.2–458.8 eV). This result indicates that the electron-rich organic ligands derived from Moac interact through robust electronic coupling with adjacent Ti sites, leading to an elevated electron density at the Ti sites. Further analysis indicates that as the Mo content increases, the Ti 2p peaks gradually shift towards lower binding energies, revealing a strong interaction between the Mo species and the TS-1 zeolite. As shown in Figure 5(a), the Mo 3d spectra exhibit two distinct characteristic peaks at 232.9 and 236.1 eV, corresponding to the Mo 3d_{5/2} and Mo 3d_{3/2} spin-orbit splitting components, respectively. Based on the literature, although the Mo in Moac@TS-1 catalysts exists in the hexavalent state (Mo^{6+}), its binding energy is lower than that of MoO_3 due to the strong electron shielding effect of the acetylacetonate ligands. This conclusively proves the conversion of MoO_3 into stable molybdenum acetylacetonate^[32]. Furthermore, the Mo binding energies are essentially unchanged across different loadings, indicating that all Mo species share a similar chemical environment and remain highly dispersed as molybdenum acetylacetonate complexes. These findings align with the results obtained from XRD, FT-IR, UV-vis, and TEM results.

2.2 Catalytic evaluations

As illustrated in Figure 6, the synthesis of styrene carbonate from CO_2 and styrene proceeds via a tandem reaction pathway consisting of two sequential steps. In the first step, styrene undergoes epoxidation in the presence of the oxidant (TBHP), generating styrene oxide as the reaction intermediate. In the second step, this intermediate reacts with CO_2 through TBAB-assisted cycloaddition to form the desired product, styrene carbonate (Path I). Nevertheless, when styrene oxide accumulates during the tandem process, several side reactions may occur. Excess styrene oxide can undergo further oxidation by TBHP to form benzaldehyde (Path II). In addition, the presence of water in the reaction system may lead to the hydrolysis of styrene oxide, producing 1-phenyl-1,2-ethanediol (Path III). Styrene oxide may also undergo additional transformations that yield minor or undetectable by-products (Path IV).

The catalytic performance of the encapsulated Moac@TS catalysts for the coupling reaction of olefins (styrene) with CO_2 to cyclic carbonates was evaluated at 70 °C and 1.0 MPa CO_2 (Figure 7(a)). using the Mo-free TS-1 zeolite as the catalyst resulted in a styrene conversion of 62.8% and a styrene carbonate selectivity of only 50.0%.

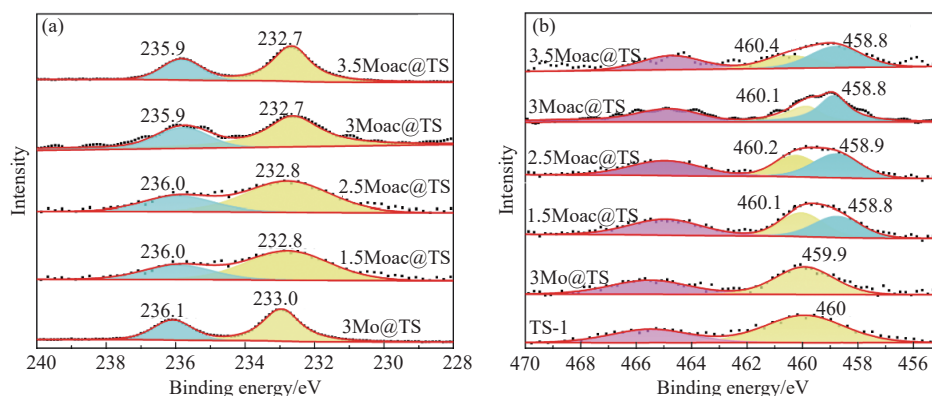


Fig. 5 Mo 3d (a) and Ti 2p (b) XPS spectra of TS-1 zeolite and the Moac@TS series catalysts

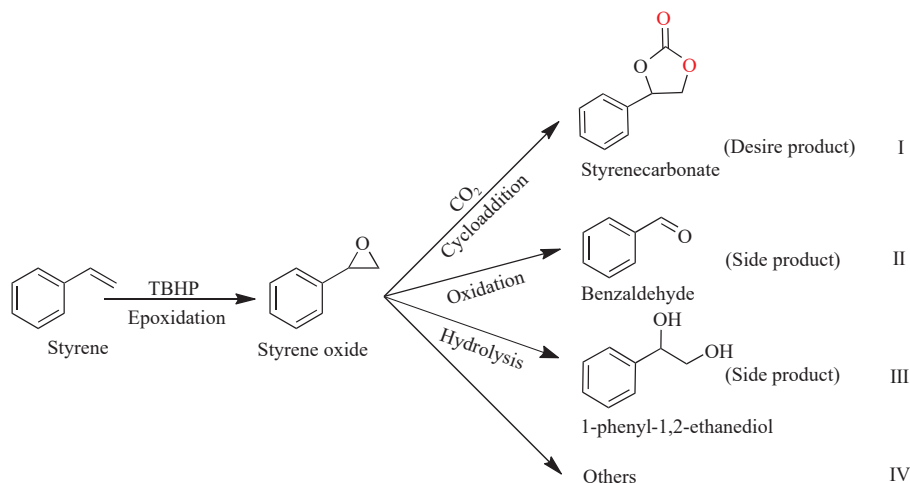


Fig. 6 Pathways of the coupling catalytic reaction between styrene and CO_2

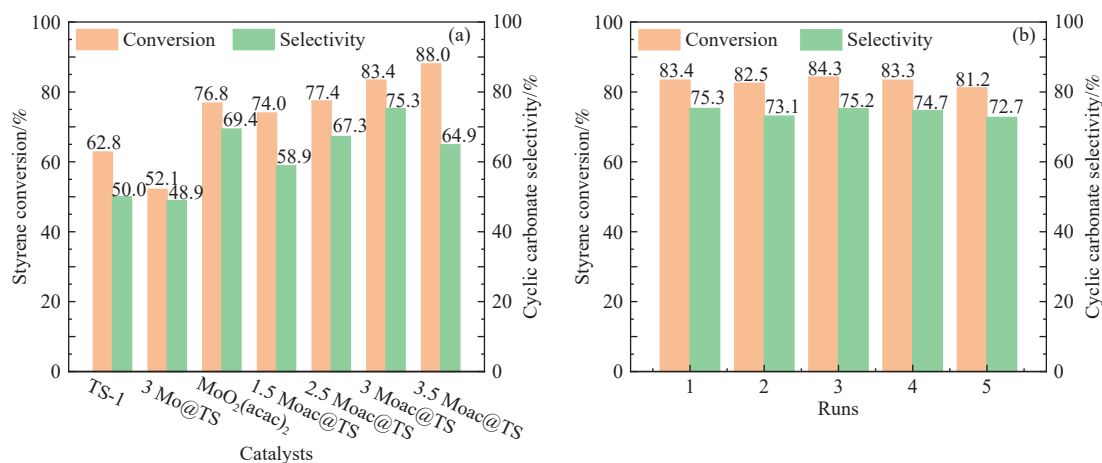


Fig. 7 Catalytic performance of TS-1 zeolite and the Moac@TS series catalysts (a) and recycling stability test results of the 3Moac@TS catalyst (b)

This suggests that the framework Ti sites in TS-1 can catalyze the epoxidation of styrene, while the co-catalyst (TBAB) promotes subsequent CO_2 cycloaddition. Specifically, the Br^- of TBAB possesses ring-opening capability, and the quaternary ammonium salt facilitates CO_2 adsorption and activation, thereby enabling formation of the cyclic carbonate. When a small amount of Mo species was incorporated during TS-1 crystallization, forming the MoO_3 -encapsulated Mo@TS sample, a moderate styrene conversion was still observed. However, partial pore blockage restricted access to Ti sites, leading to a lower styrene conversion, while the styrene carbonate selectivity decreases only slightly, confirming the key role of TBAB in the CO_2 cycloaddition step. Using molybdenum acetylacetonate alone as the catalyst (60 mg) affords a styrene conversion of 76.8% and a styrene carbonate selectivity of 69.4%, demonstrating its intrinsic activity toward this tandem reaction. Nevertheless, its homogeneous nature leads to difficult separation and high processing cost. Encapsulating molybdenum acetylacetonate inside TS-1, therefore, results in an easily recoverable heterogeneous catalyst while preserving the desirable activity of the molecular complex.

The reaction results of Moac@TS catalysts reveal that increasing the content of molybdenum acetylacetonate leads to a steady rise in styrene conversion. When the Mo content reaches 2.6%, the resulting 3Moac@TS catalyst achieves a conversion of 83.4%, and a further increase to 3.2% results in a slightly higher conversion of 88.0%. This is primarily attributed to the excellent epoxidation capability of molybdenum acetylacetonate, which works synergistically with the electron-rich Ti active sites in TS-1. In contrast to the conversion trend, the selectivity towards the styrene carbonate first increases and then decreases with increasing encapsulated Mo species content. Among them, the 3Moac@TS catalyst exhibits the optimal catalytic performance, achieving a styrene conversion of 83.4% and a styrene carbonate selectivity of 75.3%. Since the overall process proceeds via a tandem epoxidation–cycloaddition sequence, excessively high Mo contents accelerate

epoxidation beyond the rate of TBAB-mediated CO_2 cycloaddition. This results in the accumulation of the styrene oxide intermediate within the solution, which promotes side reactions (Paths II–IV, Figure 6) and ultimately reduces carbonate selectivity.

The 3Moac@TS catalyst was selected for reusability testing under identical reaction conditions. After each cycle, the catalyst was separated from the reaction mixture by high-speed centrifugation and reused directly without further regeneration. As shown in Figure 7(b), the catalyst exhibits excellent catalytic stability. After five cycles, the catalytic activity decreases slightly from 83.4% to 81.2%, and the carbonate selectivity drops from 75.3% to 72.7%, corresponding to an overall decline of less than 3%. To further evaluate structural stability, the spent catalyst after five cycles was characterized by XRD and FT-IR (Figure 8). Compared to the fresh catalyst, no significant diffraction peaks or functional group vibration bands were observed. These results confirm that the preparation strategy employed in this study effectively stabilizes the molybdenum acetylacetonate within the TS-1 zeolite structure, prevents leaching of active species during reaction, and provides a foundation for its practical application.

2.3 Catalytic mechanism of Moac@TS catalysts

To elucidate the reaction pathway for the coupling reaction of styrene and CO_2 to styrene carbonate over the encapsulated Moac@TS catalysts, the conversion behavior of styrene oxide—the key reaction intermediate—was examined using the TS-1, 3Mo@TS and 3Moac@TS. As shown in Figure 9, all three catalysts exhibit similar styrene oxide conversion and styrene carbonate selectivity, reaching approximately 90% and 80%, respectively. These results demonstrate that the co-catalyst (TBAB) primarily governs the activation of styrene oxide and the CO_2 cycloaddition step.

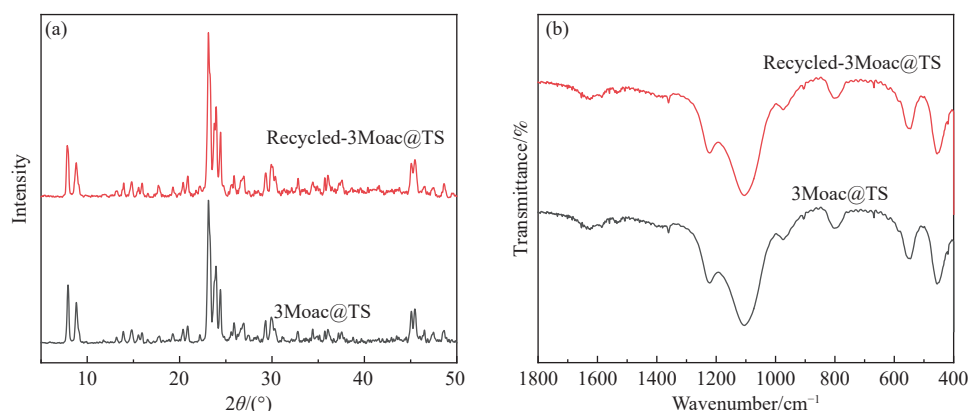


Fig. 8 XRD patterns (a) and FT-IR spectra (b) of the fresh and five-time reused 3Moac@TS catalyst

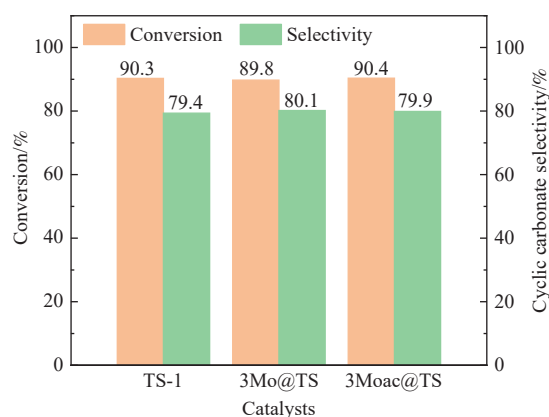


Fig. 9 Catalytic performance of TS-1, 3Mo@TS and 3Moac@TS in the preparation of cyclic carbonate from styrene oxide

However, TBAB alone is unable to ensure complete and highly selective conversion, highlighting the necessity of a controlled formation rate of styrene oxide. The rate of epoxidation, determined by the molybdenum

acetylacetonate species and the Ti sites in TS-1, must be balanced with the TBAB-mediated CO_2 cycloaddition rate. This balance explains the decline in cyclic carbonate selectivity observed at high Mo loadings, where accelerated epoxidation leads to excess accumulation of styrene oxide and consequently promotes side reactions.

Based on the structural characterization and performance analysis results, together with relevant literature reports, a plausible reaction pathway and the mechanistic roles of various catalyst components are proposed, as illustrated in Figure 10. The coupling reaction of CO_2 and styrene to produce styrene carbonate proceeds through two key stages: epoxidation followed by CO_2 cycloaddition. In the epoxidation stage, the active Ti sites in TS-1 and the molybdenum acetylacetonate species work synergistically. The Mo and Ti sites coordinate with TBHP to form highly active Mo/Ti-OOR peroxy complexes. These complexes transfer an oxygen atom to styrene via a ternary transition-state mechanism, producing styrene oxide as the crucial intermediate.

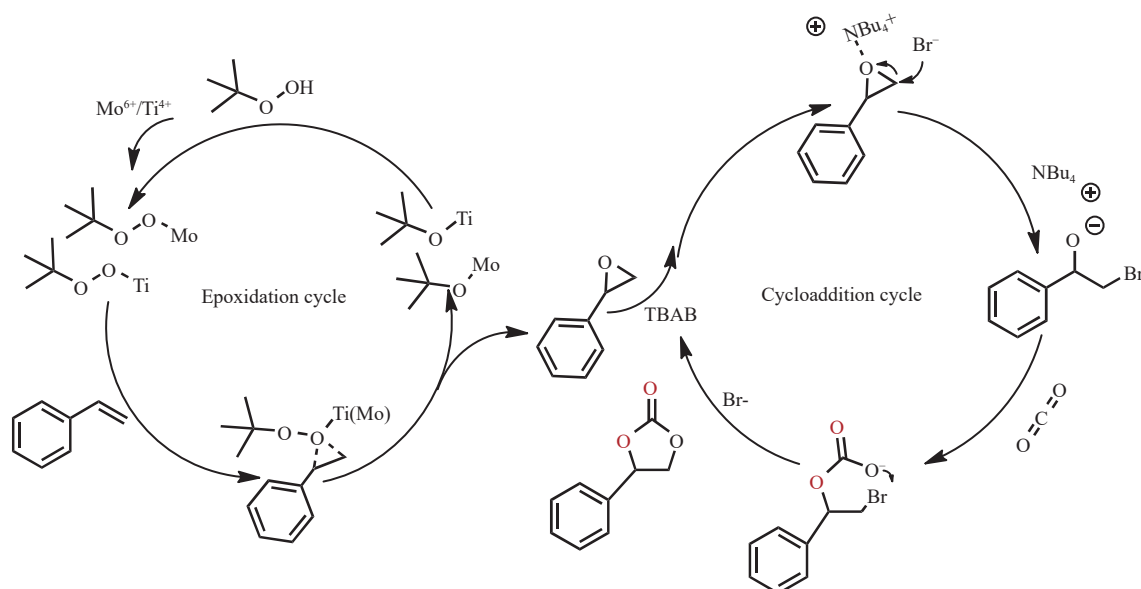


Fig. 10 Catalytic mechanism of Moac@TS catalysts for the oxycarbonylation of styrene

In the subsequent CO_2 cycloaddition step, TBAB plays a critical catalytic role. The $[\text{NBu}_4]^+$ cation of TBAB interacts with the oxygen atom of styrene oxide, activating the epoxide and facilitating the nucleophilic attack by Br^- at the less sterically hindered carbon. This leads to epoxide ring-opening and the formation of an oxyanion intermediate. The oxyanion intermediate then nucleophilically attacks the carbon atom of a CO_2 to form a cyclic intermediate, which undergoes intramolecular closure to yield styrene carbonate and regenerate Br^- , thus completing the catalytic cycle of TBAB.

3 Conclusion

In this study, molybdenum acetylacetonate was successfully encapsulated within TS-1 zeolite (Moac@TS) to construct a series of bifunctional catalysts capable of mediating the tandem epoxidation–cycloaddition process for CO_2 –olefin coupling. Comprehensive characterization results from XRD, FT-IR, UV-vis, TEM, etc., confirmed that the Mo species were stably confined inside the microporous framework as isolated molybdenum acetylacetonate complexes with high dispersion, while the intrinsic crystallinity, porosity, and tetrahedral Ti sites of TS-1 were well preserved. Electronic interaction between the encapsulated Mo species and the framework Ti atoms of TS-1 generated synergistic active centers, which played a decisive role in regulating the formation and subsequent transformation of the styrene oxide intermediate. Catalytic evaluation revealed that adjusting the Moac loading directly influences the epoxidation rate, allowing fine control over the relative rates of the two reaction steps. This kinetic balance proved essential for maximizing carbonate selectivity and minimizing side reactions associated with excess styrene oxide accumulation. The optimal catalyst exhibited stable and excellent performance over five repeated cycles under mild conditions, confirming the robustness of the encapsulated structure and the resistance of the active species to leaching. Overall, the encapsulated structured catalyst developed in this work to some extent addresses the key challenges of active species stability and reaction process matching in the CO_2 coupling with olefins reaction, thereby offering new insights for designing efficient and stable integrated catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

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乙酰丙酮钼封装在 TS-1 分子筛催化剂用于 CO_2 耦合烯烃制环碳酸酯

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摘要: CO_2 耦合烯烃制环碳酸酯具有原子经济性高、产物应用广泛等优势, 是当前可持续化学领域的研究热点。然而, 该反应过程面临环氧化和环加成催化活性位平衡失配的关键挑战。本论文采用水热合成和后处理路线, 制备了封装乙酰丙酮钼的 TS-1 分子筛催化剂, 旨在探究双功能催化反应之间的平衡匹配及其调控机制。研究结果表明, Mo 物种以高度分散的乙酰丙酮钼络合物形式稳定限域于 TS-1 分子筛结构中, 不仅与四配位 Ti 位形成电子耦合协同活性中心, 且对分子筛骨架结构和孔道性质无显著影响。在 CO_2 耦合苯乙烯制环碳酸酯反应中, 基于 Mo 含量优化, 实现了对环氧化反应的有效调控, 达到了环加成反应之间的平衡匹配。所得优选催化剂在温和条件下性能优异, 苯乙烯转化率为 83.4%, 目标产物选择性达到 75.3%, 且表现出良好的循环稳定性。本工作所制备的封装结构催化剂较好地解决了 CO_2 耦合烯烃催化反应中双功能催化转化平衡匹配和循环稳定性的关键问题, 为设计高效、稳定的集成催化剂提供了新思路。

关键词: TS-1 分子筛; 乙酰丙酮钼; 封装; CO_2 转化; 环碳酸酯

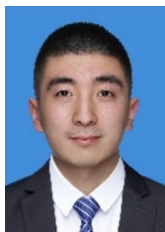
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