

Breaking the activity-selectivity trade-off in CO₂-driven N-monomethylation on a bifunctional inverse ZrZnO_x/Cu catalyst

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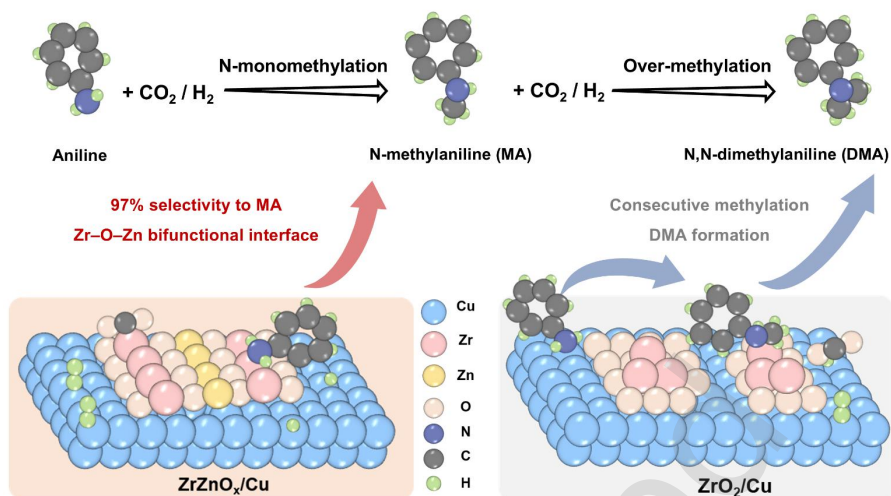
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This work reports a bifunctional inverse ZrZnO_x/Cu catalyst that enables highly selective N-monomethylation of aniline with CO_2/H_2 under mild conditions, delivering a 93% N-methylaniline yield at near-complete aniline conversion. The engineered Zr-O-Zn interface stabilizes CO_2 -derived intermediates while kinetically suppressing the consecutive MA-to-DMA methylation step, thereby breaking the activity-selectivity trade-off.

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ABSTRACT: Selective N-methylation utilizing CO₂ as a renewable C1 source offers a sustainable route to valuable amines, yet arresting the reaction at the N-monomethylation stage remains a formidable challenge. Here, we report an inverse ZrZnO_x/Cu catalyst in which Zr-O-Zn interfacial sites enable high-yield N-monomethylation under mild conditions. The optimized catalyst delivers a 93% N-methylaniline yield at near-full aniline conversion under 150 °C and 3 MPa, outperforming binary ZrO₂/Cu and commercial Cu/ZnO/Al₂O₃ catalysts. The catalyst also exhibits robust stability over ten consecutive cycles and good applicability across diverse primary amines. Mechanistic studies reveal that the bifunctional interface provides adjacent Lewis acid and basic/defect sites, stabilizes CO₂-derived oxygenated intermediates, and suppresses N-methylaniline re-adsorption and subsequent over-methylation, thereby decoupling the competing methylation steps. This work proposes a bifunctional mechanism that integrates site-blocking effects with intermediate stabilization, providing a highly efficient and stable protocol for precise C-N bond formation.

KEYWORDS: CO₂/H₂, N-monomethylation, Inverse catalyst, Zr-O-Zn site, bifunctional interface

1 Introduction

The catalytic conversion of carbon dioxide (CO₂) into a renewable C1 feedstock is an important approach to reduce the carbon footprint of chemical synthesis and support carbon neutrality targets [1, 2]. Beyond hydrogenation of CO₂ to bulk platform molecules [3-6], CO₂ has attracted growing attention as a sustainable methylating agent for C-N bond construction, enabling the production of high-value-added chemicals while improving process safety [7, 8]. In particular, N-methylation mediated by CO₂ and H₂ provides an attractive alternative to conventional methods that rely on toxic and hazardous methylation reagents such as methyl iodide and dimethyl sulfate [9, 10]. The resulting N-methylamines are prevalent motifs in pharmaceuticals, bioactive molecules, agrochemicals, dyes, and functional materials [11, 12]. Despite the distinct advantages of high atom economy and water as the sole byproduct, achieving selective N-monomethylation using CO₂ is hampered by an intrinsic conflict between activity and selectivity [13, 14]. The inertness of CO₂ necessitates harsh activation conditions [15, 16], yet the desired N-monomethylated product is more nucleophilic than the substrate, making it thermodynamically prone to over-methylation under the

same conditions [17, 18].

Catalytic systems for CO₂-driven N-methylation have progressed from homogeneous noble-metal complexes to more practical heterogeneous catalysts. Early homogeneous catalysts, typically Ru-based [19-21], offer high activity but suffer from difficulties in separation and recycling, which limits their scalability. An early heterogeneous example was reported by Du et al. in 2015, who demonstrated the direct methylation of amines with CO₂ and H₂ over supported Au catalysts, thereby establishing the feasibility of this transformation on a solid catalyst platform, although the system still relied on a noble metal [22]. In this context, heterogeneous Cu-based catalysts have become particularly attractive because Cu is earth-abundant and efficient for H₂ dissociation [23, 24]. Extensive research has focused on supporting Cu nanoparticles on various oxides to facilitate CO₂ activation and control tandem N-methylation pathways [25-27]. For example, a high-activity Cu-ZrO_x interface dispersed on SBA-15 was recently shown to enable selective N-monomethylation of amines with CO₂/H₂ [28]. Cu-ZnO/TiO₂ catalysts were also reported to exhibit excellent N-monomethylation performance. Mechanistic analysis in that work suggested a pathway involving N-phenylcarbamic acid and N-phenylformamide intermediates

over Cu-based active sites [13].

However, most reported binary Cu-based systems require pressures exceeding 5 MPa or temperatures above 180 °C to reach satisfactory yields [13, 29-32], which induce undesirable side reactions, including aromatic amine self-coupling, over-methylation, and over-hydrogenation of the aromatic ring [33]. Furthermore, the reaction mechanism remains a subject of debate, complicating rational catalyst design [32, 34-37]. In addition, a recent inverse ZrO_2/Cu catalyst featuring $\text{Zr}^{3+}\text{-O-Cu}$ interfacial sites was reported to promote CO_2 -driven N-methylation of amines through a preferential C-N coupling mechanism, bypassing the need for formate- or formaldehyde-type active intermediates [33]. These recent studies collectively indicate that the local interfacial structure not only determines catalytic efficiency, but may also redirect the dominant reaction pathway and thus the final mono-/di-methylation selectivity. Therefore, an effective catalyst should be capable of activating CO_2 under mild conditions while establishing an adsorption environment that favors the initial methylation step and suppresses the re-adsorption and further methylation of the more nucleophilic N-monomethylated product.

The inverse oxide/metal catalysts, featuring oxide nanoparticles dispersed on a metallic support, have demonstrated exceptional promise in CO_2 hydrogenation by maximizing the density of active oxide-metal interfaces [15, 38]. Notably, inverse Cu-based catalysts have achieved impressive performance in CO_2 hydrogenation [39-41]. Our previous works have elucidated that the inverse ZrO_2/Cu configuration creates abundant coordinatively unsaturated Zr sites at the metal-oxide boundary [24-26]. These distinctive interfacial sites significantly lower the activation barrier for CO_2 and stabilize critical oxygenated intermediates, thereby enabling highly efficient methanol synthesis compared with conventional Cu/oxide catalysts. Inspired by this, extending such interfacial synergy to the reductive coupling of CO_2 -derived species with amines presents a compelling prospect for precise C-N bond formation. Nevertheless, a key unresolved issue is how subtle modification of inverse Cu-based interfaces alters adsorption competition, intermediate stability, and even the preferred reaction pathway, thereby determining whether high activity can be combined with high N-monomethylation selectivity under mild conditions [42, 43].

Herein, we report an inverse ZrZnO_x/Cu catalyst prepared by the co-precipitation method, composed of ZrZnO_x mixed oxide nanoparticles loaded on a metal Cu support, which successfully breaks the activity-selectivity trade-off in the CO_2 -driven N-methylation reaction of aniline. Compared with ZrO_2/Cu and $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, this catalyst achieves a 93% yield of N-methylaniline under 150 °C and 3 MPa, indicating that high conversion can be achieved together with high N-monomethylation selectivity. Structural characterization confirms the formation of mixed oxide nanoparticles well dispersed on the Cu surface, creating a bifunctional interface. Kinetic studies show that the incorporation of Zn fundamentally alters the aniline adsorption at the Zr-O-Zn interface site, manifesting as a negative reaction order. In situ DRIFTS studies support a formate-mediated pathway involving formate-, N-

phenylformamide-, and hemiaminal-like intermediates, while kinetic analysis reveals that the second methylation step from MA to DMA is strongly suppressed on ZrZnO_x/Cu . This work presents a reliable strategy for the resource utilization of CO_2 through precise interface engineering.

2 Results and discussion

2.1 Structural and chemical characterization of the catalysts

Several typical inverse catalysts were prepared by the co-precipitation method using oxalic acid as the precipitant. The crystalline structures of the as-calcined and as-reduced catalysts were initially investigated by X-ray diffraction (XRD). As shown in Figure S1a, the XRD patterns of the calcined ZnO/Cu , ZrO_2/Cu , and ZrZnO_x/Cu catalysts exhibit characteristic diffraction peaks of CuO at 35.5° and 38.9° (PDF #80-1916). Based on the Scherrer equation, the calculated crystallite size decreases in the order of ZnO/Cu (15.1 nm) > ZrO_2/Cu (10.6 nm) > ZrZnO_x/Cu (10.1 nm), suggesting that the incorporation of Zr and Zn species effectively inhibits the growth of CuO grains during calcination. After reduction in H_2 atmosphere, the XRD patterns of three catalysts show distinct diffraction peaks at 43.3° and 50.4°, corresponding to metallic Cu, confirming the complete reduction of copper oxide (Figure S1b). The exposed metallic Cu phase offers sites for hydrogen adsorption and activation. While the reduction process induces sintering across all samples, the ZrZnO_x/Cu inverse catalyst maintains the smallest Cu crystallite size (13.3 nm). This result highlights the structural robustness of the ternary system, where the ZrZnO_x species likely act as physical spacers or anchors to suppress the agglomeration of Cu nanoparticles. In addition, no diffraction peaks of ZrO_2 are observed in the XRD patterns of both the ZrO_2/Cu and ZrZnO_x/Cu catalysts, indicating that metal oxides are amorphous or are highly dispersed.

To visualize the microscopic morphology and elemental distribution, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM), HAADF-STEM, and energy-dispersive X-ray spectroscopy (EDS) were performed on the as-reduced ZrZnO_x/Cu catalyst (Figure 1a). In the AC-HAADF-STEM image (Figure 1aI), well-resolved parallel lattice fringes with an interplanar distance of approximately 0.21 nm are unambiguously indexed to the Cu (111) facet, indicating the formation of crystalline metallic Cu nanoparticles. Notably, additional lattice fringes with d-spacings of ca. 0.26 and 0.28 nm are evident at the edge regions of the Cu lattice, as highlighted by the yellow dashed circles. Given that these spacings correspond to ZnO- and/or ZrO_2 -related crystalline planes, the occurrence of local Zr/Zn-containing oxide species is inferred. The HAADF-STEM image and corresponding EDS maps (Figure 1aII-VII) show that Cu constitutes the main particle framework, while O, Zn, and Zr signals are distributed over the same aggregate and overlap with the Cu-rich region. No large isolated Zr-rich or Zn-rich domains are evident in the mapped area, supporting the high dispersion of oxide species on or near the Cu particles. The TEM and EDS images of the ZrO_2/Cu catalyst indicate that it has a similar inverse structure (Figure S2).

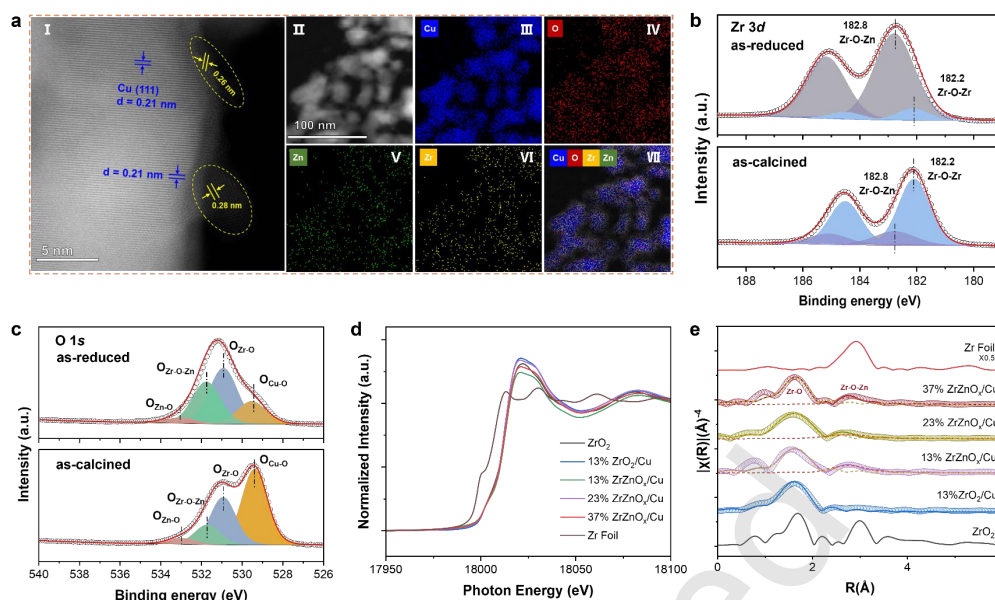


Figure 1 Structural and electronic characterization. (a) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image (I), HAADF-STEM image (II), corresponding EDS mapping of Cu, O, Zn, and Zr (III–VI), and the merged elemental mapping (VII) of the as-reduced ZrZnO_x/Cu catalyst; (b) Ambient-pressure XPS (AP-XPS) spectra of Zr 3d region over as-calcined and as-reduced ZrZnO_x/Cu catalyst; (c) AP-XPS spectra of O 1s region over as-calcined and as-reduced ZrZnO_x/Cu catalyst. (d) Zr K-edge XANES profiles and (e) Fourier-transformed Zr K-edge EXAFS spectra of Zr foil, bulk ZrO_2 , 13% ZrO_2/Cu , and ZrZnO_x/Cu catalysts with varied ZrZnO_x loadings (13%, 23%, 37%).

The dynamic evolution process of the surface electronic structure of the ZrZnO_x/Cu inverse catalyst was investigated through ambient-pressure XPS (AP-XPS). The XPS survey spectra show that the content of O element changes significantly before and after reduction, indicating a substantial change in surface oxygen species during reduction (Figure S3a). In the Cu 2p spectra, the Cu 2p_{3/2} peak of the reduced ZrZnO_x/Cu catalyst appears at 932.6 eV without intense Cu²⁺-related shake-up satellites, indicating the absence of a substantial amount of Cu²⁺ after reduction (Figure S3b). Because Cu⁰ and Cu⁺ exhibit similar Cu 2p binding energies, their relative contributions were further evaluated using the Cu LMM Auger spectrum. After reduction, the dominant Cu LMM feature is centered at approximately 918.9 eV and is assigned to metallic Cu, whereas a weaker lower-kinetic-energy contribution is attributed to a small amount of surface or interfacial Cu⁺ species (Figure S3c). The Zr 3d XPS spectra indicate that the dominant binding energy of the Zr species was observed to change from 182.2 eV (the conventional Zr⁴⁺ in ZrO_2) to 182.8 eV after reduction (Figure 1b). This suggests that the reduction treatment promotes the migration of Zn species and strengthens the electronic interaction between Zr and Zn oxides. Consistently, the O 1s spectra undergo a drastic transformation after reduction (Figure 1c). In the calcined sample, the O 1s envelope contains a strong contribution from Cu–O species, whereas after reduction the Cu–O related component is significantly weakened and the oxygen species associated with Zr–O–Zn and Zr–O environments become dominant.

Further, Zr K-edge XANES/EXAFS was introduced to clarify the local coordination environment (Figures 1d–e and Table S1). The Zr K-edge XANES spectra of ZrZnO_x/Cu shift to lower photon energy relative to bulk ZrO_2 , indicating a modified/electron-enriched Zr environment after Zn incorporation. FT-EXAFS spectra display a Zr–O first-shell feature for all oxide-containing samples, while only the Zn-containing ZrZnO_x/Cu catalysts show a distinct Zr–Zn

scattering contribution at ca. 2.7 Å (phase-uncorrected). EXAFS fitting gives Zr–O–Zn distances of 3.16–3.18 Å, supporting the presence of Zn atoms in the second coordination shell of Zr through Zr–O–Zn linkages rather than a simple physical mixture of isolated ZrO_2 and ZnO phases. In addition, EPR measurements were conducted to probe defect sites in the catalysts. A characteristic signal at $g = 2.003$, assigned to oxygen-vacancy-related defects, was observed for all samples, with ZrZnO_x/Cu showing the highest intensity, indicating that Zn incorporation increases the concentration of such defect species (Figure S4). These results indicate that Zn incorporation into the inverse ZrO_2/Cu system generates the Zr–O–Zn interface and increases oxygen-vacancy defect sites, which are closely related to the adsorption and activation behavior in CO₂-driven N-methylation.

2.2 Catalytic performance and optimization of inverse catalysts

The N-methylation of aniline (AN) with CO₂ and H₂ proceeds via a consecutive pathway, in which the initially formed N-methylaniline (MA) can undergo further methylation to produce N,N-dimethylaniline (DMA), as illustrated in Figure 2a. Achieving high yields of the monomethylated product therefore requires a catalyst that can effectively activate CO₂ while suppressing the secondary methylation of MA. Under the reaction conditions of 3.0 MPa CO₂/H₂ and 150 °C, the ZrZnO_x/Cu catalyst was compared with various representative catalysts to preliminarily evaluate the role of the inverse interface.

Both the commercial Cu/ZnO/Al₂O₃ catalyst and ZnO/Cu inverse catalyst exhibit inefficient catalytic performance in N-methylation reaction using CO₂ as C1 source (Figure 2b). ZrO_2/Cu catalyst still faces the typical activity-selectivity trade-off, where improved conversion is often accompanied by a loss of MA selectivity. In contrast, the inverse ZrZnO_x/Cu catalyst achieves both high aniline conversion and high MA

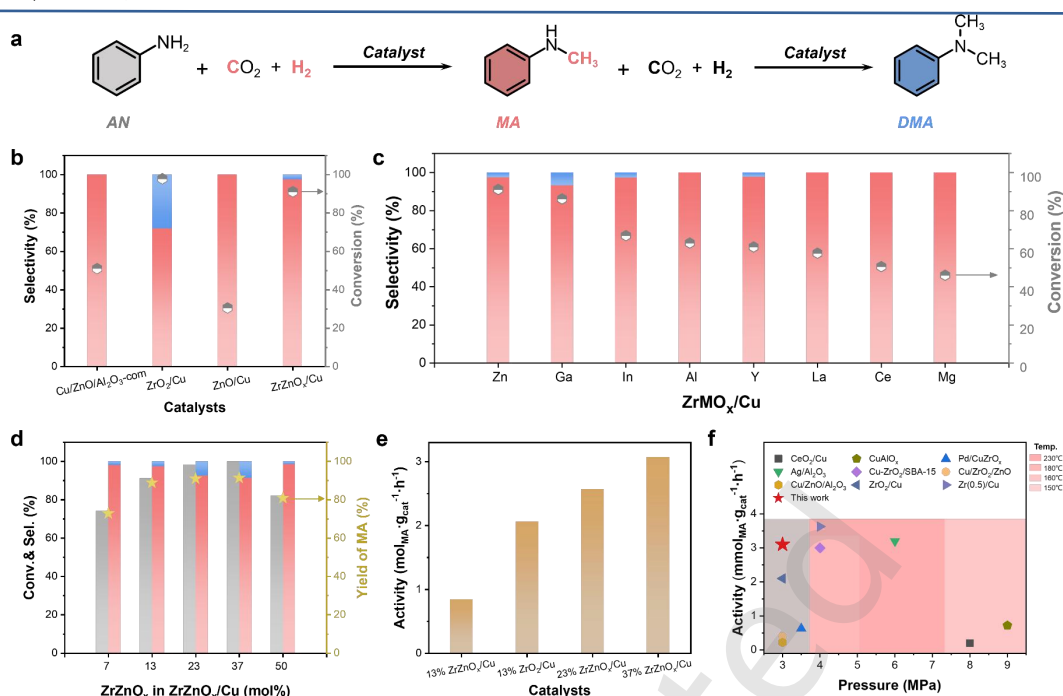


Figure 2 The N-methylation performance of catalysts. (a) Possible products in the N-methylation reaction of AN and CO_2/H_2 ; (b) Comparison of commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3\text{-com}$) and inverse ZnO/Cu , ZrO_2/Cu and ZrZnO_x/Cu ; (c) Comparison of the ZrMO_x/Cu inverse catalysts (molar ratio, $\text{Zr}:\text{M}:\text{Cu}=9:4:87$). (d) The N-methylation performance over varied ZrZnO_x/Cu inverse catalysts with different content of ZrZnO_x . Reaction conditions: 100 mg catalyst, 0.2 mmol AN, 3.0 MPa $\text{CO}_2/\text{H}_2/\text{N}_2$ (24%/72%/4%), 150 °C, 9 h, 0.2 mmol m-xylene as internal standard; (e) Activity of N-methylation over different inverse Cu-based catalysts. Reaction conditions: 50 mg catalyst, 0.2 mmol AN, 3.0 MPa $\text{CO}_2/\text{H}_2/\text{N}_2$, 150 °C, 0.2 mmol m-xylene as internal standard; (f) Comparison of the N-methylation activity of the catalyst reported [28, 29, 31, 33, 44, 45] and this work. Because these catalytic systems were tested under non-identical reaction conditions, including temperature, pressure, reaction time, and catalyst loading, the comparison is provided only for general performance context.

selectivity, highlighting the unique advantage of the Zr-O-Zn interface in suppressing over-methylation. Additional control experiments using metallic Cu, ZrZnO_x , and conventional Cu/ZrZnO_x further confirm the importance of the inverse oxide/metal architecture (Figure S5). Metallic Cu and ZrZnO_x alone exhibit much lower aniline conversion, whereas conventional Cu/ZrZnO_x shows improved but still inferior performance compared with inverse ZrZnO_x/Cu . To further optimize the catalyst composition, a series of inverse ZrMO_x/Cu catalysts (where $\text{M} = \text{Zn}, \text{Ga}, \text{In}, \text{Al}, \text{Y}, \text{La}, \text{Ce}, \text{Mg}$) were screened (Figure 2c). The choice of the secondary metal oxide significantly influenced the catalytic performance. Among the candidates, the ZrZnO_x/Cu catalyst stood out, delivering the highest AN conversion while maintaining 97% selectivity of MA.

Optimization of the catalyst composition was further conducted by varying the ZrZnO_x content (Figure 2d). The measured metal loading by ICP-OES was closely aligned with the theoretical value (Table S2). As the copper loading decreases, the intensity of the characteristic XRD peaks of CuO significantly reduces, which is in line with expectations (Figure S6). The volcano-type dependence on ZrZnO_x loading suggests that the optimum at 37% ZrZnO_x/Cu arises from a balance between metallic Cu exposure and oxide/metal interfacial-site density. At low oxide loading, the number of interfacial sites is insufficient for efficient C-N coupling, whereas excessive oxide coverage likely decreases Cu exposure and interface accessibility. As a result, 37% ZrZnO_x/Cu provides the best compromise under the present conditions.

To accurately assess the intrinsic catalytic performance, the reaction was conducted with AN conversion maintained below 20%, and the activity was calculated based on MA yield. The 37% ZrZnO_x/Cu catalyst demonstrated the highest

intrinsic activity ($3.2 \text{ mmol}_{\text{MA}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$), which was approximately four times that of the 13% ZrZnO_x/Cu sample (Figure 2e). This is attributed to the formation of more ZrZnO_x mixed oxides, which increases the acidic and basic sites in the catalyst. Following the identification of 37% ZrZnO_x/Cu as the optimal catalyst, the reaction parameters were systematically optimized, including temperature, total pressure, and reactant ratio (Figures S7-S9). The evaluation revealed that 150 °C offers the optimal trade-off between activity and selectivity, as elevated temperatures induced the formation of the over-methylated byproduct DMA. Regarding pressure and gas ratio, the conversion plateaued at 3 MPa and peaked at a stoichiometric H_2/CO_2 ratio of 3:1. Notably, a further increase in the hydrogen proportion leads to a decline in the reaction rate, attributed to the kinetic limitation caused by the reduced partial pressure of CO_2 . Consequently, standard conditions of 150 °C, 3 MPa, and $\text{H}_2/\text{CO}_2 = 3:1$ were established for all subsequent investigations. The competitiveness of the optimized ZrZnO_x/Cu catalyst is highlighted in Figure 2f. Although these literature systems were evaluated under different temperatures, pressures, reaction times, and catalyst loadings, the comparison qualitatively shows that ZrZnO_x/Cu can deliver high N-methylaniline productivity under relatively mild conditions.

The catalytic stability of the optimal ZrZnO_x/Cu inverse catalyst was then evaluated under these optimized conditions (Figure S10). During the N-monomethylation reaction of CO_2 and AN, ZrZnO_x/Cu showed no significant loss of activity over ten cycles, with a yield of approximately 90% each cycle. The STEM and EDS images of the spent ZrZnO_x/Cu catalyst show that Zr and Zn remain well dispersed after recycling (Figure S11). The XRD patterns before and after the reaction show no significant changes,

and metallic Cu remains the dominant crystalline phase (Figure S12). The spent catalyst XPS and Cu LMM Auger spectra further indicate that the ZrZnO_x environment is largely preserved and that metallic Cu remains the dominant Cu species, although a small amount of surface oxidation may occur during catalyst handling in air (Figure S13). ICP-OES analysis of the fresh catalyst, spent catalyst, and post-reaction liquid phase shows negligible metal leaching (Table S3), supporting the heterogeneous nature and structural durability of the catalyst.

Table 1. N-methylation of different amines with CO₂/H₂ catalyzed by ZrZnO_x/Cu^a

Entry	Substrate	Product	Conv. (%)	Sel. (%)
1			94.0	97.1
2			93.7	96.2
3			100	93.5
4			91.9	97.6
5			100	97.8
6			100	90.2
7			95.2	87.1
8			83.7	99.9

^a Reaction conditions: 100 mg catalyst, 0.2 mmol substrate, 150 °C, 6 h, 15 mL n-hexane, 3 MPa CO₂ and H₂ (H₂/CO₂/N₂ = 72/24/4).

The broad applicability of the optimized protocol was assessed by extending the scope to a diverse range of amine substrates (Table 1 and Figures S14-S19). Specifically, substrates equipped with electron-donating substituents (e.g., -CH₃, -OCH₃, and -nBu) delivered excellent reactivity with high N-monomethylation selectivity over 93%. It is worth noting that the catalyst showed high tolerance towards electron-withdrawing groups (e.g., -F) and sterically hindered substrates (e.g., o-toluidine), maintaining conversion levels comparable to unsubstituted aniline. The versatility of the system was further highlighted by its successful application to challenging aliphatic and heterocyclic amines. These results underscore the potential of ZrZnO_x/Cu as a versatile tool for fine chemical synthesis.

2.3 Surface properties and kinetic origins of chemoselectivity

A comparative investigation of the surface acidity, basicity, and reaction kinetics was conducted for the ZrZnO_x/Cu and ZrO₂/Cu catalysts to clarify the origins of their differing activity and product selectivity. As shown in Figures S20a and S20b, all catalysts display three CO₂ desorption peaks in the 50-650 °C range, attributed to weak, moderate, and strong basic sites. It is noted that the 37% ZrZnO_x/Cu catalyst possesses the highest density of strong basic sites, which are typically considered unfavorable for CO₂ hydrogenation (Figure S20c) [25]. Yet, it exhibits the highest activity rate of N-methylation, suggesting that CO₂ hydrogenation is likely not the rate-limiting step. The NH₃-TPD profiles reveal a striking difference in surface acid density (Figure 3a and S20d). Since desorption below 100 °C is generally attributed to physical adsorption, only the adsorption peaks above this temperature were compared. The ZrZnO_x/Cu catalyst exhibits a remarkably high adsorption capacity of approximately 2.4 mmol·g⁻¹, which is more than threefold that of ZrO₂/Cu (0.7 mmol·g⁻¹). This enhanced acidity, attributed to the incorporation of Zn species, suggests a stronger interaction between the catalyst surface and the basic substrates.

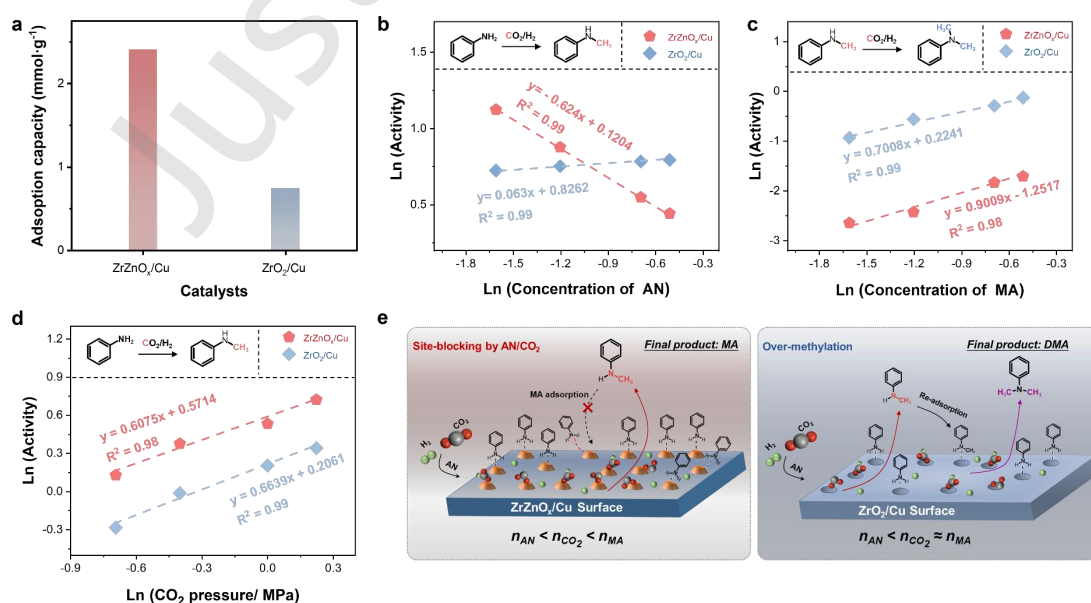


Figure 3 Kinetic and adsorption site studies. (a) Adsorption capacity of NH₃-TPD on the ZrO₂/Cu and ZrZnO_x/Cu catalysts. Double-logarithmic plots used to determine the apparent reaction orders: (b) MA formation activity versus AN concentration; (c) DMA formation activity versus MA concentration; (d) catalytic activity calculated by MA yield and CO₂ concentration; (e) A schematic diagram of the adsorption and desorption processes

To distinguish the types of acid sites, pyridine-adsorbed FTIR (Py-FTIR) was further performed (Figure S21 and Table S4). Both ZrO_2/Cu and ZrZnO_x/Cu mainly contain Lewis acid sites, represented by the band at ca. 1445 cm^{-1} , while Brønsted acid sites at ca. 1540 cm^{-1} are much less abundant. Compared with ZrO_2/Cu , ZrZnO_x/Cu shows higher Lewis acid-site amounts at all desorption temperatures and retains more Lewis acid sites after elevated-temperature desorption, indicating that Zn incorporation increases both the number and thermal stability of Lewis acid sites. Since aniline is a basic molecule, these Lewis acid sites are assigned as the main adsorption sites responsible for the strengthened aniline adsorption on ZrZnO_x/Cu . Meanwhile, CO_2 adsorption is associated mainly with surface basic oxygen species and oxygen-vacancy-related defect sites on the oxide overlayer. Thus, the Zr-O-Zn interface provides adjacent Lewis acid and basic sites, while metallic Cu supplies H_2 activation/hydrogenation sites.

The reaction orders of AN, MA and CO_2 over ZrO_2/Cu and ZrZnO_x/Cu catalysts were calculated from concentration-dependent experiments performed in the kinetic range using at least four data points (Figure S22). Figure 3b presents the dependence of the N-methylation rate on the AN concentration over the inverse catalysts. For the ZrO_2/Cu catalyst, the reaction order is 0.06, indicating that the surface coverage of AN is low and does not inhibit the reaction rate. In contrast, the ZrZnO_x/Cu catalyst exhibits a negative reaction order of -0.62. This negative dependence suggests substantially stronger adsorption of AN on the ZrZnO_x/Cu surface, leading to higher substrate coverage under the reaction conditions. Combined with NH_3 -TPD and Py-FTIR, this behavior is consistent with the enhanced Lewis acidity induced by Zn incorporation. Although the negative reaction order does not directly establish the origin of chemoselectivity, it supports a competitive adsorption scenario in which strongly adsorbed AN can disfavor the re-adsorption of the monomethylated product MA.

The kinetic behavior of the consecutive methylation step is further reflected in the dependence of the DMA formation rate on MA concentration (Figure 3c). Both catalysts show positive reaction orders with respect to MA concentration (0.90 for ZrZnO_x/Cu and 0.70 for ZrO_2/Cu). On ZrZnO_x/Cu , however, the strong competitive adsorption of AN-derived species may make MA re-adsorption less favorable and thus suppress the conversion of MA to DMA. Conversely, the weak interaction of AN with ZrO_2/Cu allows for easier re-adsorption and subsequent N-methylation of MA, resulting in lower selectivity toward the N-monomethylation product. The dependence on CO_2 pressure showed fractional positive orders of 0.61 and 0.66 for ZrZnO_x/Cu and ZrO_2/Cu , respectively (Figure 3d). These apparent reaction orders are broadly consistent with the adsorption trends indicated by CO_2 -TPD, NH_3 -TPD, and Py-FTIR.

The superior N-monomethylation selectivity of ZrZnO_x/Cu is rationalized by a competitive adsorption mechanism driven by surface acidity and basicity, as shown in Figure 3e. The negative reaction order with respect to AN corroborates the high acid density, indicating strong substrate adsorption and saturation of active sites. The reaction order for CO_2 is lower than that for MA, especially over ZrZnO_x/Cu , suggesting different sensitivities of the two steps to the surface availability of CO_2 -derived species and MA. These kinetic results suggest that strongly adsorbed AN-derived species, together with CO_2 -derived intermediates formed on basic/defect sites, can competitively disfavor MA re-adsorption. Consequently, the generated MA is kinetically hindered from undergoing over-methylation to DMA. In contrast, the weaker adsorption competition on ZrO_2/Cu permits facile MA re-adsorption and conversion to DMA. Thus, the Zn-modified inverse interface modulates the adsorption hierarchy and contributes to high N-monomethylation selectivity.

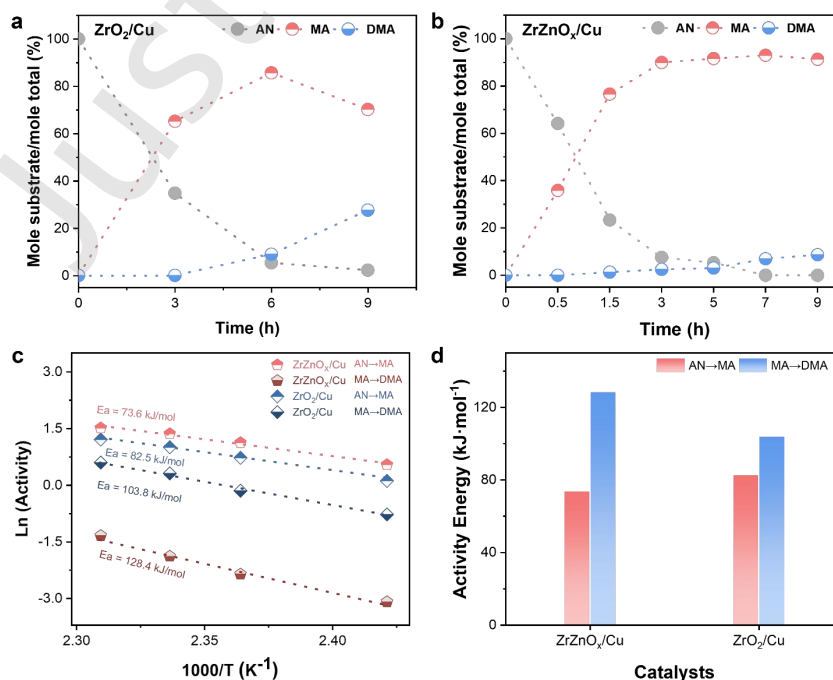


Figure 4 Time-dependent selectivity for N-methylation of AN over (a) the ZrO_2/Cu and (b) ZrZnO_x/Cu catalysts for 9 h. Reaction conditions: 50 mg catalyst, 0.2 mmol AN, 3.0 MPa $\text{CO}_2/\text{H}_2/\text{N}_2$ (24%/72%/4%), 150 °C, 0.2 mmol m-xylene as internal standard; (c) Arrhenius plots for N-methylation of

AN and MA over ZrO_2/Cu and ZrZnO_x/Cu catalysts; (d) Apparent activation energy of N-methylation of AN or MA over ZrO_2/Cu and ZrZnO_x/Cu catalysts.

To validate the proposed kinetic model and further understand the reaction pathway, we monitored the temporal evolution of the product distribution over both catalysts. The reaction on ZrO_2/Cu follows a typical consecutive pathway. The yield of the intermediate MA reaches a maximum at approximately 6 hours, after which it notably declines, accompanied by a rapid increase in DMA selectivity to over 20% (Figure 4a). This confirms that on the unmodified surface, the intermediate MA is susceptible to further over-methylation. In contrast, the ZrZnO_x/Cu catalyst exhibits a distinctly stable product profile (Figure 4b). The concentration of MA increases steadily and plateaus at a high yield (>90%) without significant consumption to form DMA, even after prolonged reaction times to 9 hours. This distinct kinetic behavior highlights a superior temporal processing window compared to the ZrO_2/Cu catalyst. Unlike conventional systems where the reaction time must be strictly controlled to prevent the subsequent conversion of MA to DMA, the ZrZnO_x/Cu catalyst can confine the reaction to the N-monomethylation stage. This observation aligns well with the kinetic results discussed above, suggesting that the transformation of MA to DMA is effectively suppressed on the Zn-modified surface.

Temperature-dependent kinetic measurements were conducted, allowing the energetic origins of this selectivity

to be quantified (Figure S23). The Arrhenius plots and the corresponding activation energies reveal a decisive energetic disparity between the two reaction steps (Figures 4c-d). For the primary methylation step, the ZrZnO_x/Cu catalyst exhibits a modestly lower activation energy ($E_a = 73.6 \text{ kJ}\cdot\text{mol}^{-1}$) than ZrO_2/Cu ($E_a = 82.5 \text{ kJ}\cdot\text{mol}^{-1}$), which accounts for the enhanced AN-to-MA activity. However, a reverse trend is observed for the secondary methylation step. The activation barrier for over-methylation of MA on ZrZnO_x/Cu increases dramatically to $128.4 \text{ kJ}\cdot\text{mol}^{-1}$, whereas it remains relatively moderate on ZrO_2/Cu ($103.8 \text{ kJ}\cdot\text{mol}^{-1}$). Therefore, the improved selectivity of ZrZnO_x/Cu originates primarily from the kinetic suppression of the second methylation step rather than simply from facilitation of the first step.

Collectively, the high MA selectivity of the ZrZnO_x/Cu catalyst stems from a synergistic mechanism that kinetically impedes MA re-adsorption through preferential coverage by AN-derived species and CO_2 -derived intermediates, while energetically imposing a substantially higher activation barrier for the second methylation step. This dual action effectively blocks the second pathway to DMA formation.

2.4 Mechanistic Investigation via in Situ DRIFTS and Control Experiments

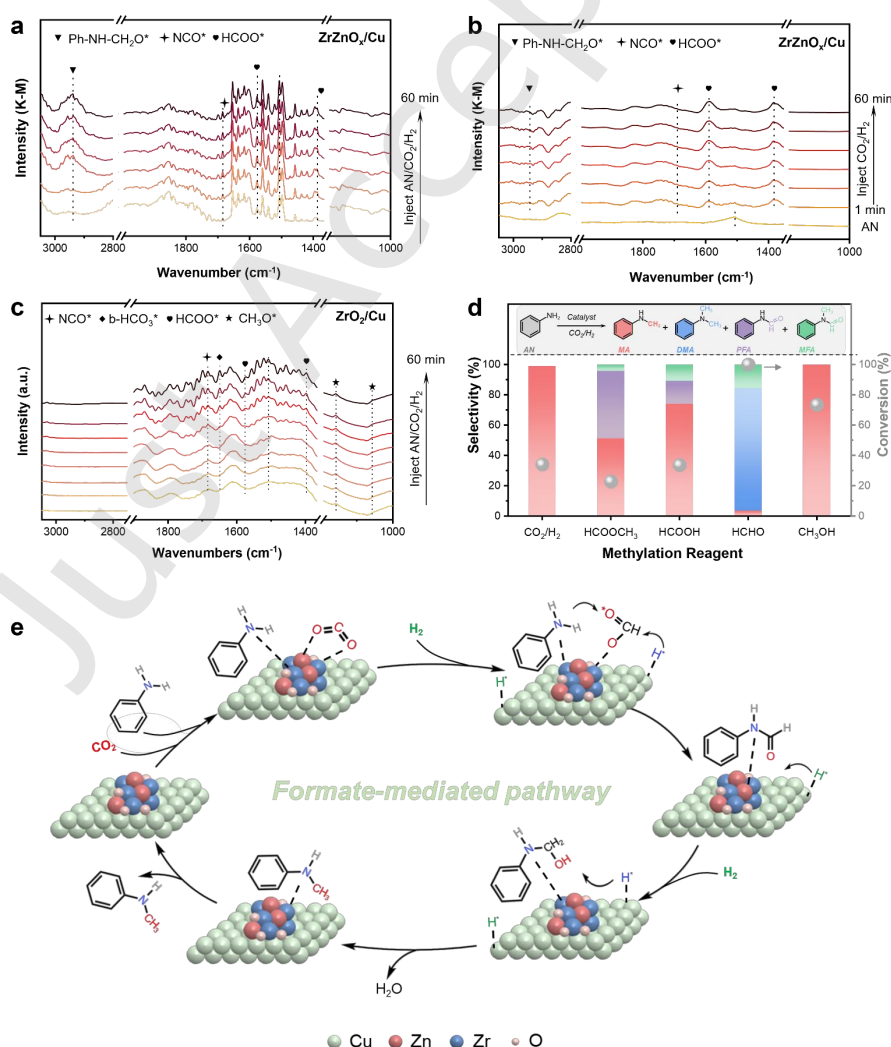


Figure 5 Mechanism investigation experiments. (a) In situ DRIFTS spectra on ZrZnO_x/Cu , co-introducing $\text{CO}_2/\text{H}_2/\text{N}_2$ and AN; (b) In situ DRIFTS spectra on ZrZnO_x/Cu , introduction of AN vapor followed by switching to $\text{CO}_2/\text{H}_2/\text{N}_2$; (c) In situ DRIFTS spectra on ZrO_2/Cu , co-introducing $\text{CO}_2/\text{H}_2/\text{N}_2$ and AN. (d) Product distributions in the N-methylation of AN using different C_1 sources. Reaction conditions: 150 μL C_1 source, 0.2 mmol AN, 150 $^\circ\text{C}$, 0.5 h. For

the CO₂ route, 3.0 MPa H₂/CO₂/N₂ (72/24/4). (e) Possible reaction mechanism over the ZrZnO_x/Cu catalyst for CO₂-driven N-methylation of AN.

To investigate the reaction pathway for N-methylation of AN with CO₂/H₂ over the ZrO₂/Cu and ZrZnO_x/Cu inverse catalysts, a series of in-situ DRIFTS experiments were systematically conducted under the following conditions: (i) introduction of AN followed by switching to CO₂/H₂; (ii) co-introduction of AN and CO₂/H₂; and (iii) pre-exposure to CO₂/H₂ followed by introduction of AN.

Under the co-feeding condition of CO₂/H₂ and AN over the ZrZnO_x/Cu catalyst, the spectra exhibit bands associated with adsorbed aniline-derived species and CO₂-derived oxygenated intermediates (Figure 5a). The bands at ca. 1387 and 1575 cm⁻¹ are assigned to formate-related species [46]. The band at ca. 1684 cm⁻¹ is assigned to N-phenylformamide-like species (NCO*), and the C-H stretching feature around 2935 cm⁻¹ is associated with oxygenated hemiaminal-like intermediates [25, 34, 47]. To better show their temporal evolution, normalized intensities of representative bands were extracted after baseline correction and added as Figure S24. The formate-related band increases rapidly at the initial stage and then reaches a plateau, while the NCO* band increases more gradually, supporting a formate-mediated pathway on ZrZnO_x/Cu.

When AN vapor was first introduced onto the ZrZnO_x/Cu catalyst, a pronounced band at ca. 1506 cm⁻¹ was observed, which can be assigned to the skeletal vibration of adsorbed aniline species, confirming the adsorption and activation of AN on the catalyst surface (Figure 5b). After switching to CO₂/H₂, formate-related species gradually appeared, followed by the evolution of N-phenylformamide-like and hemiaminal-like species. This sequential evolution from adsorbed AN/formate species to PFA and then to hemiaminal-like intermediates supports a cascade pathway in which surface formates couple with adsorbed AN to generate PFA, followed by hydrogenation to form hemiaminal-like intermediates before yielding the final product. Conversely, in the reverse sequence where AN was introduced to a formate-saturated surface (Figure S25), the gradual formation of PFA and hemiaminal species was also observed. Collectively, these in situ experiments disfavor a solely direct C-N coupling pathway and support a formate-mediated pathway under the present conditions.

Comparing the spectroscopic signatures of the two catalysts reveals the structural origin of their selectivity differences (Figure 5c). While the ZrO₂/Cu catalyst also facilitates the initial formation of PFA, no clear hemiaminal-related band around 2935 cm⁻¹ is observed under the same co-feeding conditions. Instead, distinct bands at ca. 1158 and 1056 cm⁻¹, assignable to methoxy-like species, are more evident on ZrO₂/Cu. This difference suggests that Zn incorporation changes the dominant surface C1-species evolution: formate/PFA/hemiaminal-related species are more persistent on ZrZnO_x/Cu, whereas methoxy-like species are more readily accumulated on ZrO₂/Cu. Such behavior is consistent with the time-dependent product evolution and the higher tendency toward over-methylation observed on ZrO₂/Cu.

C1 source screening experiments further help to evaluate possible reaction intermediates and side pathways (Figure 5d). Only MA was identified as the product of the CO₂-driven N-methylation reaction when AN exhibited a low conversion. When formic acid (HCOOH) or methyl formate

(HCOOCH₃) was used as the methylation reagent, considerable amounts of PFA and MFA were observed even at AN conversion below 40%, indicating the occurrence of over-methylation. Formaldehyde (HCHO) exhibited high reactivity but poor selectivity, yielding predominantly over-methylated DMA, which excludes free formaldehyde as the key intermediate for selective N-monomethylation. Methanol (CH₃OH) gave high AN conversion and MA selectivity, suggesting that methanol or methanol-derived oxygenated C1 species can serve as efficient alkylating intermediates when upstream CO₂ hydrogenation steps are bypassed. A D₂ isotope-labeling experiment afforded 94.9% AN conversion and 98.9% monomethylation selectivity, with GC-MS showing clear deuterium incorporation in the molecular-ion region (Figure S26). This result supports molecular hydrogen as the hydrogen source for formation of the N-methyl group.

Based on the sequential integration of spectroscopic and kinetic evidence, we propose the reaction mechanism depicted in Figure 5e. Metallic Cu sites are assigned mainly to H₂ dissociation and hydrogenation, while the Zr-O-Zn interface provides Lewis acid/basic sites for aniline adsorption, CO₂-derived formate stabilization, and subsequent C-N coupling. Aniline preferentially adsorbs on Lewis acid sites, and CO₂ is activated on basic or oxygen-vacancy sites to form formate species. Formate-derived C1 species then couple with adsorbed aniline to form N-phenylformamide intermediates, followed by hydrogenation/dehydration steps toward MA. The re-adsorption and further methylation of MA are suppressed by strong competitive adsorption of aniline-derived species and by the higher apparent barrier for MA-to-DMA conversion.

3 Conclusions

In summary, this work breaks the intrinsic activity-selectivity trade-off in CO₂-driven N-monomethylation via rational interfacial engineering of an inverse ZrZnO_x/Cu catalyst. Beyond delivering a 93% yield of N-methylaniline at near-full conversion under mild conditions, the optimized catalyst exhibits good catalytic stability over ten cycles and a reasonably broad substrate scope. This performance advantage is attributed to its ability to effectively decouple the sequential methylation steps, and thus prevents the over-methylation pathway that dominates on binary ZrO₂/Cu catalysts. The underlying mechanism originates from a bifunctional interface that provides adjacent Lewis acid/basic sites, stabilizes key CO₂-derived oxygenated intermediates, and kinetically suppresses MA re-adsorption and over-methylation. These results underscore interfacial engineering as a generalizable platform for steering cascade selectivity in CO₂ valorization, offering a transferable strategy for precise C-N bond formation and other cascade reactions in sustainable C1 chemistry.

Electronic Supplementary Material: Supplementary material, including experimental details, additional characterization results, catalytic tests, kinetic data, and in situ DRIFTS spectra, is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909128>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare no competing interests.

Author contribution statement

Yaqi Wang: Data curation, formal analysis, validation. Xiangxin Jin, Ying Tang, Chengxi Feng: Validation. Shurui Fan: Conceptualization, visualization, writing manuscript. Siwei Li, Lili Lin: Project administration, conceptualization, writing manuscript, funding acquisition. All the authors have approved the final manuscript.

Informed consent

Not applicable

Ethics statement

Not applicable

Use of AI statement

None.

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Electronic Supplementary Material

Breaking the activity-selectivity trade-off in CO₂-driven N-monomethylation on a bifunctional inverse ZrZnO_x/Cu catalyst

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Contents:

1. Experimental Section

2. Supplementary Figures and Tables

Figure S1. The XRD patterns of (a) the as-calcined ZrO_2/Cu , ZnO/Cu and ZrZnO_x/Cu ; (b) the as-reduced ZrO_2/Cu , ZnO/Cu and ZrZnO_x/Cu inverse catalysts.

Figure S2. TEM of ZrO_2/Cu catalysts; (b-d) HRTEM images with corresponding EDS mappings of ZrO_2/Cu catalyst.

Figure S3. (a) XPS survey; (b) Cu 2p ;(c) Cu LMM Auger electron spectrum of as-calcined or as-reduced ZrZnO_x/Cu catalysts.

Table S1. EXAFS fitting parameters of Zr K-edge for reference samples (Zr foil, ZrO_2) and ZrO_2/Cu , ZrZnO_x/Cu catalysts.

Figure S4. EPR spectra of ZnO/Cu , ZrO_2/Cu , and ZrZnO_x/Cu catalysts.

Table S2. The Cu, Zn and Zr content of the fresh catalysts.

Figure S5. Catalyst performance evaluation of Cu, ZrZnO_x , Cu/ZrZnO_x and ZrZnO_x/Cu .

Figure S6. XRD patterns of different oxide contents of ZrZnO_x/Cu inverse catalysts.

Figure S7. The effect of reaction temperature on the catalytic performance of 37% ZrZnO_x/Cu .

Figure S8. The effect of reaction pressure on the catalytic performance of 37% ZrZnO_x/Cu .

Figure S9. The effect of reactant gas ratio on the catalytic performance of 37% ZrZnO_x/Cu .

Figure S10. Experimental results of recycling 37% ZrZnO_x/Cu catalyst.

Figure S11. STEM and EDS spectra of the ZrZnO_x/Cu -spent catalyst.

Figure S12. The XRD pattern of the fresh and spent ZrZnO_x/Cu inverse catalyst.

Figure S13. XPS spectra of the ZrZnO_x/Cu -spent catalyst. (a) Zr 3d; (b) O 1s; (c) Cu 2p; (d) Cu LMM Auger electron spectrum.

Table S3. The Cu, Zn and Zr content of the catalysts and liquid products.

Figure S14. GC-MS spectrum of N-methylation reaction of p-methylaniline with CO_2/H_2 .

Figure S15. GC-MS spectrum of N-methylation reaction of p-methoxyaniline with CO_2/H_2 .

Figure S16. GC-MS spectrum of N-methylation reaction of p-Fluoroaniline with CO_2/H_2 .

Figure S17. GC-MS spectrum of N-methylation reaction of 4-Butylaniline with CO_2/H_2 .

Figure S18. GC-MS spectrum of N-methylation reaction of 2-Aminopyridine with CO_2/H_2 .

Figure S19. GC-MS spectrum of N-methylation reaction of n-Decylamine with CO_2/H_2 .

Figure S20. (a) CO_2 -TPD profiles of ZrO_2/Cu and ZrZnO_x/Cu catalysts; Adsorption capacity of CO_2 -TPD on the ZrO_2/Cu and ZrZnO_x/Cu catalysts at (b) 450-650 °C and (c) 50-450 °C; (d) NH_3 -TPD profiles of ZrO_2/Cu and ZrZnO_x/Cu catalysts.

Figure S21. Pyridine-adsorbed FTIR spectra of ZrO_2/Cu and ZrZnO_x/Cu after desorption at 150, 250, and 350 °C.

Table S4. The results of Py-FTIR of ZrO_2/Cu and ZrZnO_x/Cu catalyst.

Figure S22. Concentration-dependent reaction performance for the stepwise methylation of aniline over ZrZnO_x/Cu and ZrO_2/Cu catalysts.

Figure S23. Temperature-dependent reaction performance for the stepwise methylation of aniline over ZrZnO_x/Cu and ZrO_2/Cu catalysts.

Figure S24. Normalized intensities of representative in situ DRIFTS bands under CO_2/H_2 and aniline co-feeding conditions over ZrZnO_x/Cu .

Figure S25. In situ DRIFTS spectra on ZrZnO_x/Cu after CO_2/H_2 introduction followed by switching to AN vapor.

1. Experimental Section

1.1 Chemicals and Materials

All chemicals were used as received without further purification. Copper nitrate trihydrate (AR, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), zirconium nitrate pentahydrate (AR, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), zinc nitrate hexahydrate (AR, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), oxalic acid (99 wt%, Macklin Co., Ltd.), Methanol (AR, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), formic acid (AR, 98%, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), formaldehyde solution (37% -40%, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), aniline (AR, 99.5%, Aladdin Co., Ltd.), N-methylaniline (99%, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), meta xylene (AR, China National Pharmaceutical Group Chemical Reagent Co., Ltd.), N,N-dimethylaniline (99.5%, Macklin Co., Ltd.)

1.2 Catalyst preparation

The ZrMO_x/Cu inverse catalysts ($M = \text{Zn, Ga, In, Al, Y, La, Ce, Mg}$, with $\text{Cu mol\%} > 50\%$) were synthesized by an oxalate co-precipitation method. Take the ZrZnO_x/Cu catalyst with a molar ratio of 9:4:87 as an example. The oxalic acid was used as a precipitating agent. In a typical synthesis procedure: 0.02 mol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.002 mol $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and 0.001 mol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursors were dissolved in 100 mL ethanol. Under vigorous stirring at room temperature, 100 mL of 0.5 M oxalic acid in ethanol solution was added dropwise to the mixture at a flow rate of 1 mL/min. After continuous stirring for 2 h, the resultant solid was separated by centrifugation, washing with ethanol, and drying at 70 °C for 12 h. The obtained powder was calcined at 400 °C for 3 h in a muffle furnace. After cooling to room temperature, the powder was subjected to heat treatment at 300 °C using a programmed U-tube furnace with the temperature increased at a ramp rate of 5 °C/min and holding at 300 °C for 2 h under a 5% H_2/N_2 .

ZnO/Cu and ZrO_2/Cu were also synthesized following the same procedure, except that only the corresponding metal nitrate solutions were added.

1.3 Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded with a PANalytical X'Pert PRO powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). The working voltage was 40 kV and the working current was 40 mA. The patterns were collected with a 2θ range from 10° to 80° at a step of 0.0167°. The average crystallite sizes of the samples were calculated with the Scherrer equation based on the strongest hkl diffraction peak of CuO or Cu .

The loading contents of Zr, Zn and Cu were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Varian 720).

CO_2 temperature programmed desorption (CO_2 -TPD) measurements were performed using a Bel mass spectrometer. The samples were treated in 5% H_2/Ar at 300 °C for 2 h (ramping rate 5 °C/min), followed by flushing with Ar for 30 min before being cooled to 50 °C. CO_2 adsorption was performed in 10% CO_2/He for 60 min, after which the samples were flushed with Ar for 40 min to remove the un-adsorbed CO_2 . Then, the CO_2 desorption was performed. The heating rate was set as 10 °C/min. A mass spectrometer (Bel mass) was used to detect the desorbed CO_2 .

The scanning transmission electron microscopy (STEM) analysis was conducted using Nion UltraSTEM-100 electron microscopy operated at 60 kV. The Z-contrast images were collected with an annular dark field detector in the range of 75-210 mrad with a convergence angle of 32 mrad on Nion. Electron energy-loss spectroscopy was carried out with the same experimental set-up with a probe current of about 50 pA. The samples for electron microscopy characterization were dispersed in ethanol and then drop-cast onto holey carbon-coated gold grids.

The ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) measurements were performed on an Axis Supra photoelectron spectrometer (Kratos Analytical Ltd.) using a monochromatized $\text{Al K}\alpha$ radiation. The catalyst powders were pressed on a tantalum plate and then loaded into the AP-XPS chamber. The sample was first reduced with 20 mL/min 10% H_2 at 300 °C for 2 h and cooled down to room temperature. XPS spectra of the Zr 3d, Zn 2p, Cu 2p, Cu LMM, O 1s, and C 1s regions were acquired under both fresh and reduced conditions.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were carried out using an FTIR spectrometer of Bruker Vertex 80 equipped with a Harrick cell and an MCT detector. The spectra were expressed in units of Kubelka-Munk (K-M). Typically, the catalyst sample was reduced in the IR cell with 5% H_2/Ar at 300 °C for 2 h (ramping rate 5 °C/min), then cooled to 150 °C under Ar (99.999% purity) atmosphere. The background spectra were collected under the N_2 atmosphere. Subsequently, 10 mL min^{-1} of AN vapor was introduced into the IR cell for 1 h. The IR cell was then purged with N_2 for 1 h to remove free and physically adsorbed AN. After that, 10 mL min^{-1} of CO_2/H_2 was passed into the IR cell and FTIR spectra were collected. For different feed-sequence experiments, AN vapor and CO_2/H_2 were introduced either sequentially or simultaneously.

Pyridine-adsorbed Fourier-transform infrared spectroscopy (Py-FTIR) was performed on a Nicolet 6700 instrument equipped with a mercury cadmium telluride detector at ambient pressure. Before pyridine adsorption, the catalyst sample was pretreated under vacuum at 150 °C to remove physically adsorbed water and surface impurities. After cooling to room temperature, pyridine vapor was introduced into the IR cell until adsorption saturation was reached. The weakly adsorbed pyridine molecules were then removed by evacuation. Subsequently, the sample was heated and evacuated at 150, 250, and

350 °C, respectively, and the corresponding FTIR spectra were collected after each desorption step.

The Zr K edge XAFS spectra of the catalysts were performed at BL14W beamline of the Beijing Synchrotron Radiation Facility (BSRF). Before the measurement, the samples were pressed into tablet. All XAFS spectra were processed using the IFEFFIT package. The EXAFS oscillations were fitted according to back-scattering equation, using the FEFF models generated from crystal structures of ZrO_2 .

1.4 Catalyst evaluation

N-monomethylation of AN: N-methylation experiments were carried out in a stainless-steel autoclave (Laibei AE100) equipped with a pressure control system and an automatic temperature controller. In a typical process, 100 mg catalyst, 0.2 mmol AN, and 15 mL n-hexane were added to the autoclave. Then, the stainless-steel autoclave was purged with CO_2 and H_2 ($\text{H}_2/\text{CO}_2/\text{N}_2 = 72/24/4$, molar ratio) for five times to remove residual air. After that the stainless-steel autoclave was pressurized to 3 MPa with CO_2 and H_2 again. The resulting mixture was vigorously stirred with a stirring rate of 800 rpm at a given temperature for certain reaction time. At the end of the experiment, the autoclave was cooled to room temperature in a water bath. 0.2 mmol m-xylene was added as the internal standard. The liquid mixture was filtered with 0.22 μm nylon membrane, and the resulting liquid products were analyzed by gas chromatography (GC, Agilent 8860). The gas chromatograph was equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD), an HP-5 column (0.32 mm in diameter, 30 m in length) and an HP-INNOWAX column (0.32 mm in diameter, 30 m in length).

The conversion of AN (χ_{AN}) and the yield of expected product N-methylaniline (MA) were determined by:

$$\chi_{\text{AN}}(\%) = \frac{AN_{\text{feed}}(\text{mol}) - AN_{\text{residue}}(\text{mol})}{AN_{\text{feed}}(\text{mol})} \times 100\%$$

$$\text{Yield}_{\text{MA}}(\%) = \frac{MA(\text{mol})}{AN_{\text{feed}}(\text{mol})} \times 100\%$$

The activities of MA, DMA were determined by:

$$\text{Activity}_{[\text{Product}]} = \frac{n_{\text{Product}}}{m_{\text{Catalyst}} \times \text{time}} (\text{mmol} \cdot \text{g}_{\text{Catalyst}}^{-1} \cdot \text{h}^{-1})$$

N-monomethylation of other amines: the reaction conditions were as follows: 100 mg catalyst, 0.2 mmol substrate and 15 mL n-hexane. The reactions were performed in an autoclave purged with 3 MPa of CO_2 and H_2 at 150 °C. After the reaction, the liquid mixture was filtered with a 0.22 μm nylon membrane. Quantification was performed by GC-FID using m-xylene as an internal standard, while product identities were confirmed by GC-MS (5977C GC/MSD) equipped with HP-5 capillary column (0.32 mm in diameter, 25 m in length).

Kinetic test: the reaction conditions were as follows: 0.2 mmol AN, 0.2 mmol m-xylene as the internal standard, and 15 mL n-hexane. The reactions were performed in an autoclave purged with 3 MPa of CO_2 and H_2 at a certain temperature. Reaction conversion was controlled in the kinetic range.

D_2 Isotope-Labeling Experiment. In a typical experiment, 100 mg the ZrZnO_x/Cu catalyst, 0.2 mmol aniline, and 15 mL n-hexane were loaded into a stainless-steel autoclave. After removal of residual air, the autoclave was charged to a total pressure of 3.0 MPa with $\text{D}_2/\text{CO}_2/\text{N}_2$ at room temperature. The reaction was conducted at 150 °C for 3 h with vigorous stirring at 800 rpm. After completion of the reaction, the autoclave was cooled to room temperature, and 0.2 mmol of m-xylene was added as an internal standard. The products were quantified by GC-FID, and the isotopic composition of the monomethylated product was further analyzed by GC-MS.

2. Supplementary Figures and Tables

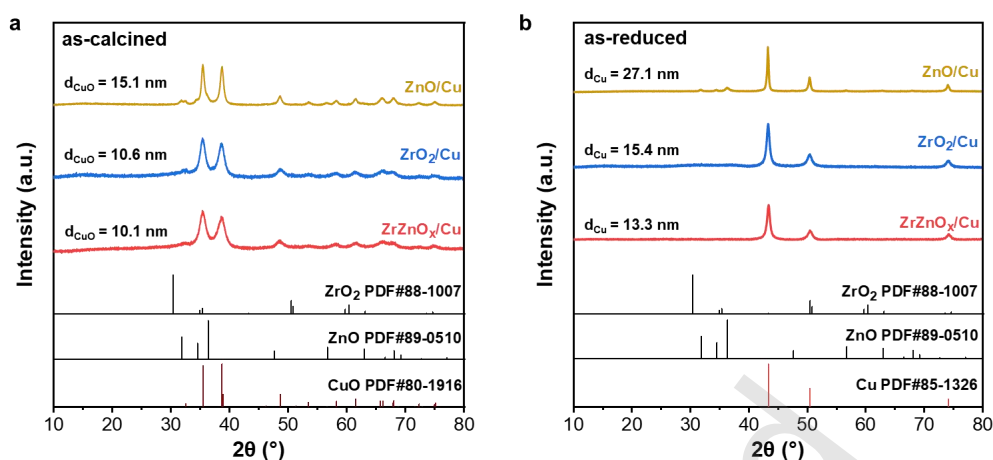


Figure S1. The XRD patterns of (a) the as-calcined ZrO_2/Cu , ZnO/Cu and ZrZnO_x/Cu ; (b) the as-reduced ZrO_2/Cu , ZnO/Cu and ZrZnO_x/Cu inverse catalysts.

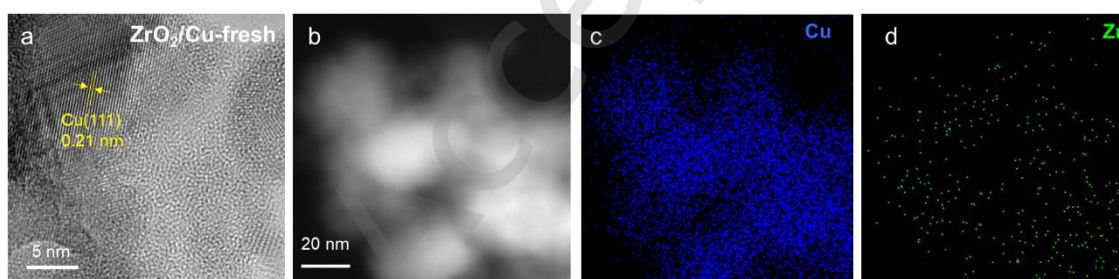


Figure S2. (a) TEM image of ZrO_2/Cu catalysts; (b-d) HRTEM images with corresponding EDS mappings of ZrO_2/Cu catalyst.

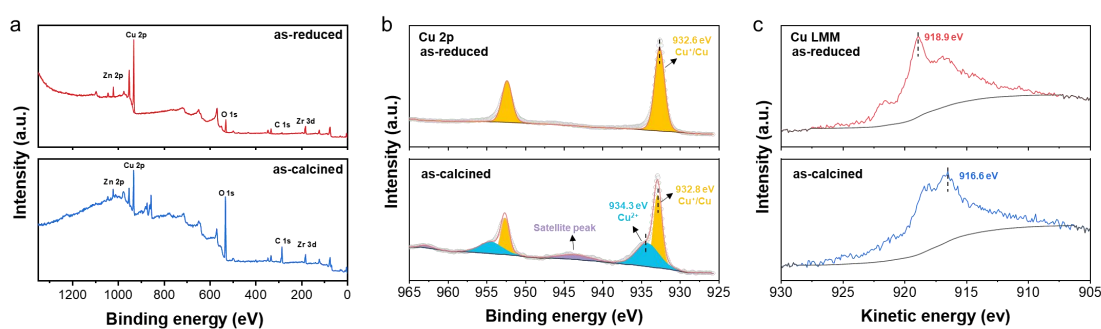
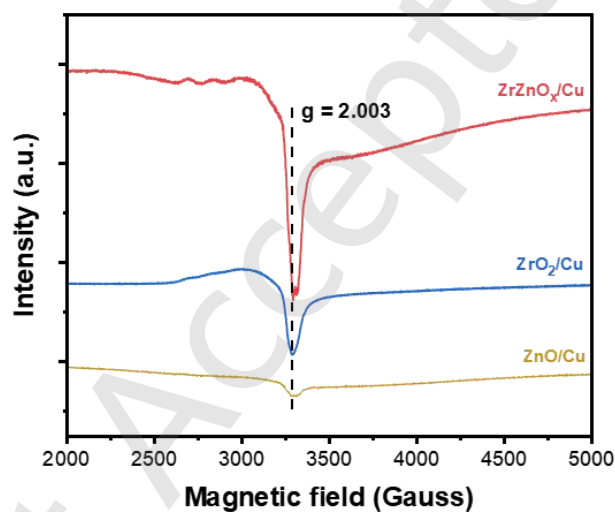


Figure S3. (a) XPS survey; (b) Cu 2p; (c) Cu LMM Auger electron spectrum of as-calcined or as-reduced ZrZnO_x/Cu catalysts.

Table S1. EXAFS fitting parameters of Zr K-edge for reference samples (Zr foil, ZrO₂) and ZrO₂/Cu, ZrZnO_x/Cu catalysts ^a

Sample	Shell	R (Å) ^a	C.N. ^b	ΔE ₀ (eV) ^c	σ ² (*10 ⁻³ Å ²) ^d	S ₀ ^{2e}	R factor (*10 ⁻³)
13% ZrO ₂ /Cu	Zr-O	2.17±0.01	7.8±0.3	-0.4±0.4	9.0		6.6
13% ZrZnO _x /Cu	Zr-O	2.18±0.02	6.5±0.3	0.7±0.5	9.4	0.86	18.5
	Zr-O-Zn	3.17±0.03	1.9±0.5		7.1		
23% ZrZnO _x /Cu	Zr-O	2.17±0.02	7.4±0.4	-0.2±0.6	9.1		12.9
	Zr-O-Zn	3.18±0.05	1.5±0.6		7.1		
37% ZrZnO _x /Cu	Zr-O	2.17±0.01	6.7±0.3	0.1±0.5	9.3		11.5
	Zr-O-Zn	3.16±0.03	1.4±0.4		7.1		
Zr foil	Zr-Zr	3.22±0.01	12	5.3±0.6	8.7	0.86±0.06	8.5

^a. Bond length; ^b. Average coordination number; ^c. Difference of potential of sample and standard; ^d. Debye-Waller factor; ^e. Amplitude reduction factor;

**Figure S4.** EPR spectra of ZnO/Cu, ZrO₂/Cu, and ZrZnO_x/Cu catalysts.**Table S2.** The Cu, Zn and Zr content of the fresh catalysts ^a

Catalysis	Zr:Zn:Cu (molar ratio)	Cu loading _a (wt%)	Zr loading _a (wt%)	Zn loading _a (wt%)
ZrZnO _x /Cu	5:2:93	72.6	4.4	1.8
ZrZnO _x /Cu	9:4:87	66.1	8.9	3.5
ZrZnO _x /Cu	15:8:77	55.9	15.8	5.6
ZrZnO _x /Cu	25:12:63	41.1	23.1	8.8
ZrO ₂ /Cu	13:0:87	63.8	12.9	-
ZnO/Cu	0:13:87	68.7	-	10.3

^a The concentration of Cu, Zr and Zn was measured by ICP-OES.

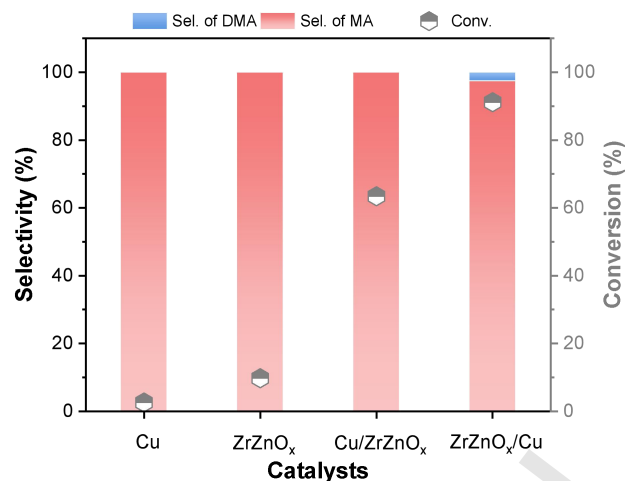


Figure S5. Catalyst performance evaluation of Cu, ZrZnO_x, Cu/ZrZnO_x and ZrZnO_x/Cu.

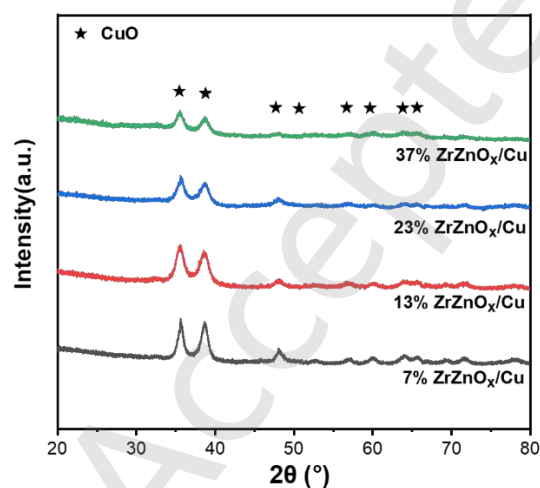


Figure S6. XRD patterns of different oxide contents of ZrZnO_x/Cu inverse catalysts.

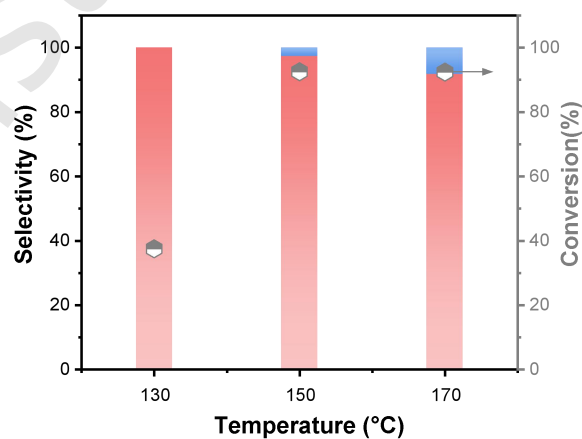


Figure S7. The effect of reaction temperature on the catalytic performance of 37% ZrZnO_x/Cu. Reaction conditions: 100 mg catalyst, 15 mL n-hexane, 3 MPa CO₂/H₂, 0.2 mmol AN, 3 h, 0.2 mmol m-xylene as internal standard.

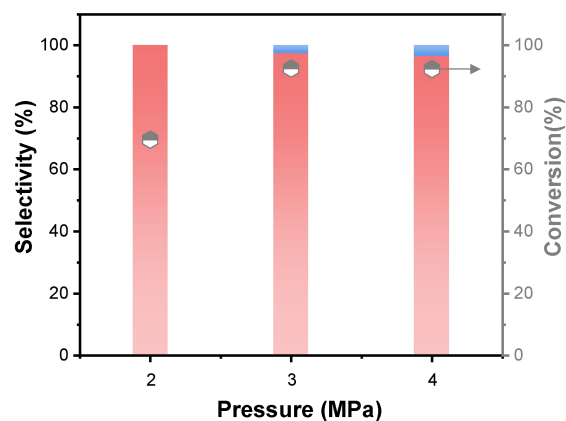


Figure S8. The effect of reaction pressure on the catalytic performance of 37% ZrZnO_x/Cu. Reaction conditions: 100 mg catalyst, 15 mL n-hexane, 0.2 mmol AN, 150 °C, 3 h, 0.2 mmol m-xylene as internal standard.

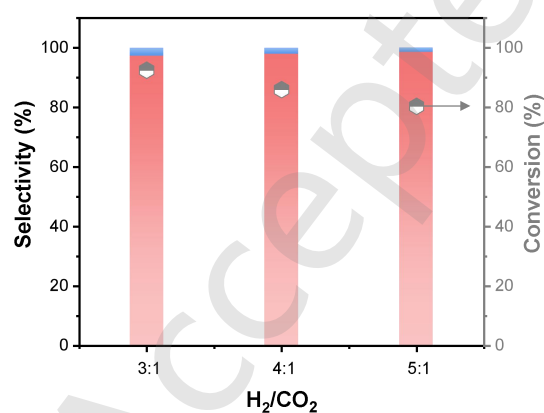


Figure S9. The effect of reactant gas ratio on the catalytic performance of 37% ZrZnO_x/Cu. Reaction conditions: 100 mg catalyst, 15 mL n-hexane, 3 MPa CO₂/H₂, 0.2 mmol AN, 150 °C, 3 h, 0.2 mmol m-xylene as internal standard.

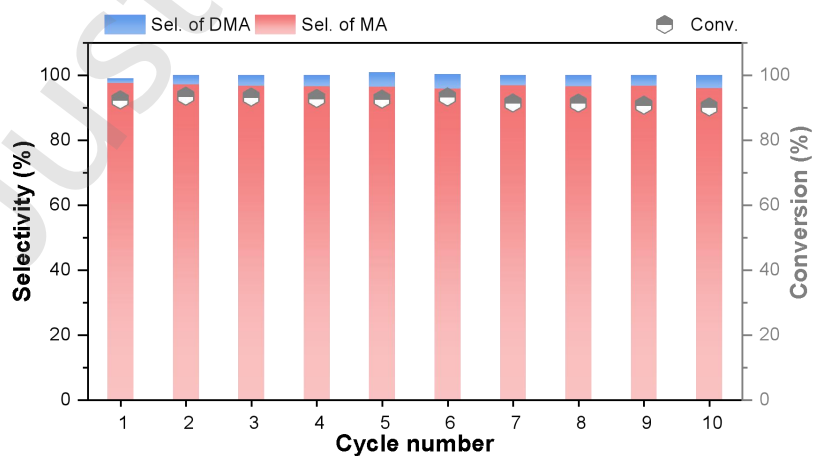


Figure S10. Experimental results of recycling 37% ZrZnO_x/Cu catalyst. Reaction conditions: 100 mg catalyst, 0.2 mmol AN, 15 mL n-hexane, 3 MPa CO₂/H₂, 150 °C, 3 h, 0.2 mmol m-xylene as internal standard.

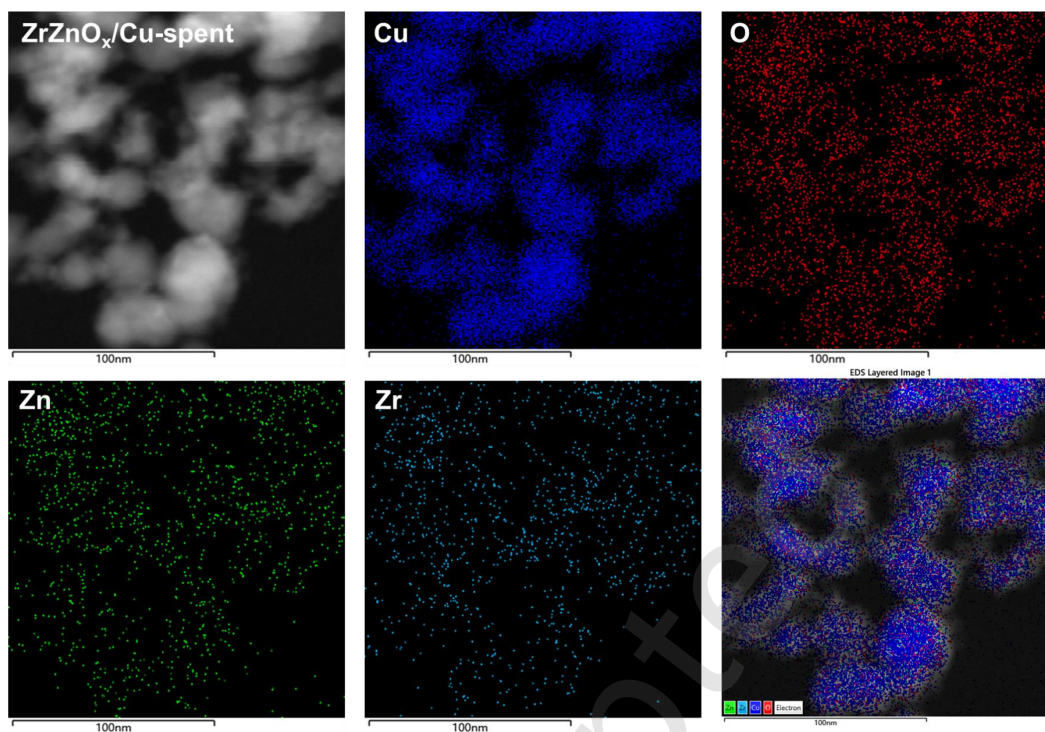


Figure S11. STEM and EDS spectra of the ZrZnO_x/Cu -spent catalyst.

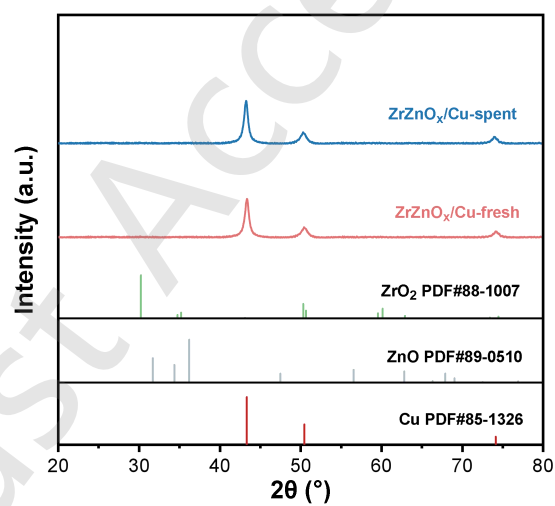


Figure S12. The XRD pattern of the fresh and spent ZrZnO_x/Cu inverse catalyst.

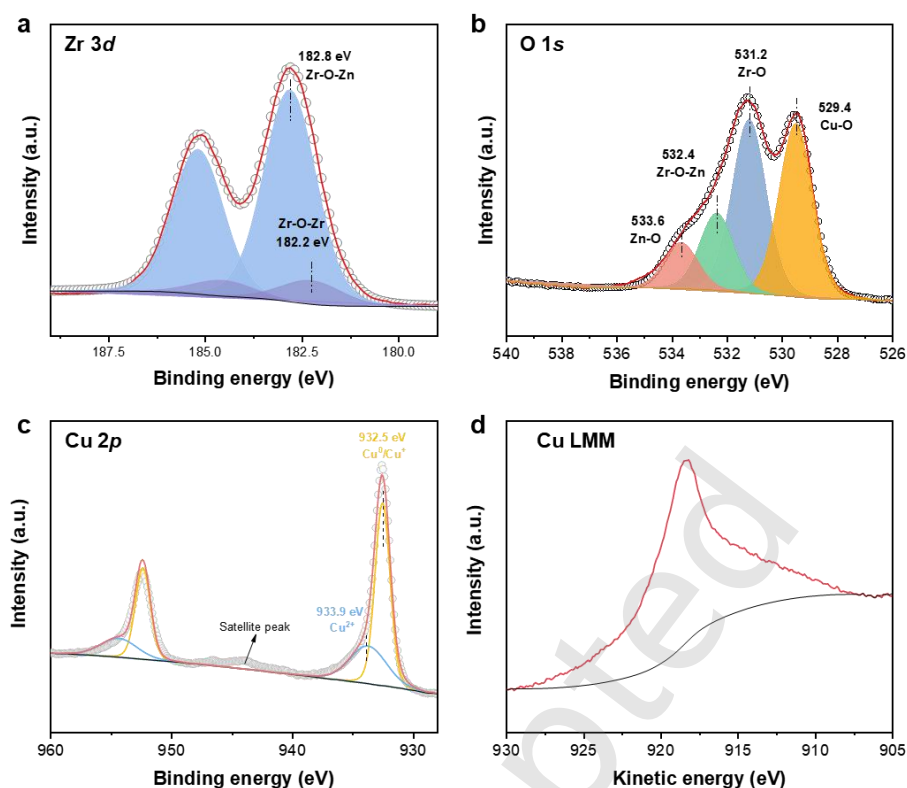


Figure S13. XPS spectra of the ZrZnO_x/Cu-spent catalyst. **(a)** Zr 3d; **(b)** O 1s; **(c)** Cu 2p; **(d)** Cu LMM Auger electron spectrum.

Table S3. The Cu, Zn and Zr content of the catalysts and liquid products ^a

Entry	Catalyst	Loading / Concentration in liquid phase (wt%)		
		Cu	Zr	Zn
1	ZrZnO _x /Cu-fresh	41.1	23.1	8.8
2	ZrZnO _x /Cu-spent	41.1	23.1	8.8
3	Liquid products after reaction	Not detected	Not detected	Not detected

^a The metal contents of the catalyst were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

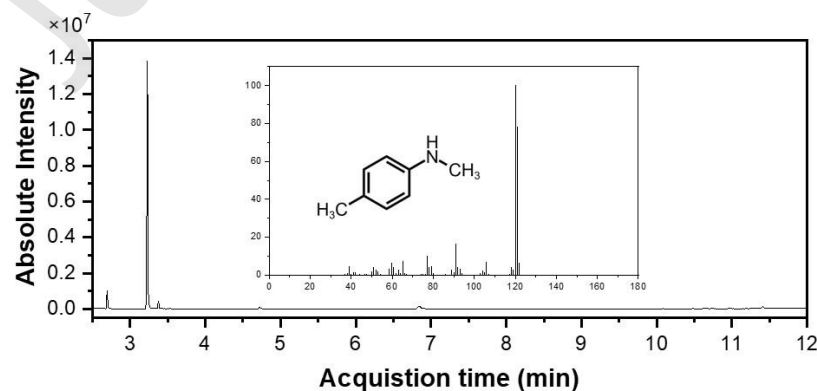


Figure S14. GC-MS spectrum of N-methylation reaction of p-methylaniline with CO₂/H₂.

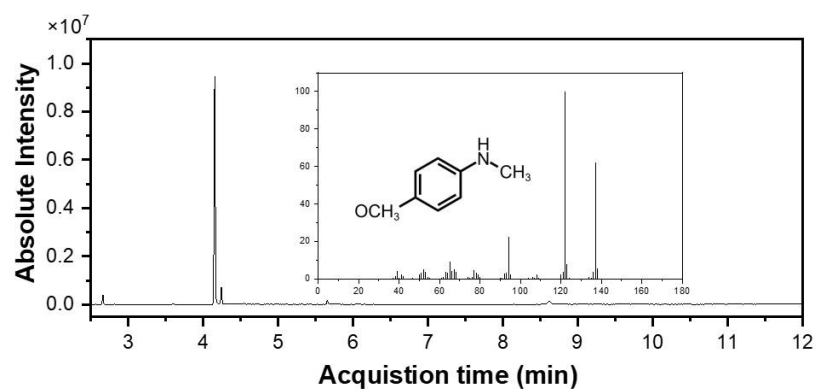


Figure S15. GC-MS spectrum of N-methylation reaction of p-methoxyaniline with CO_2/H_2 .

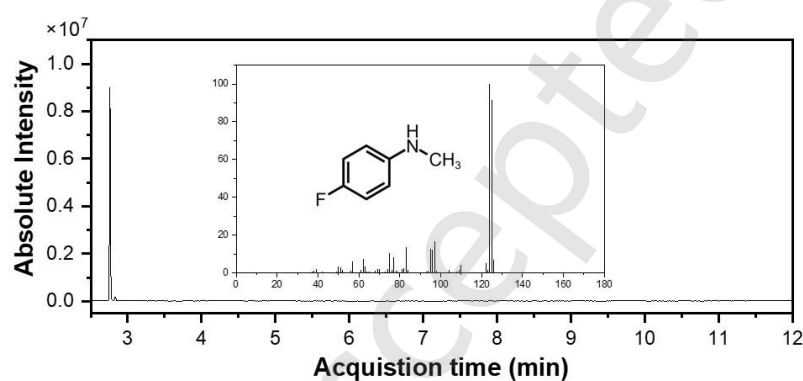


Figure S16. GC-MS spectrum of N-methylation reaction of p-fluoroaniline with CO_2/H_2 .

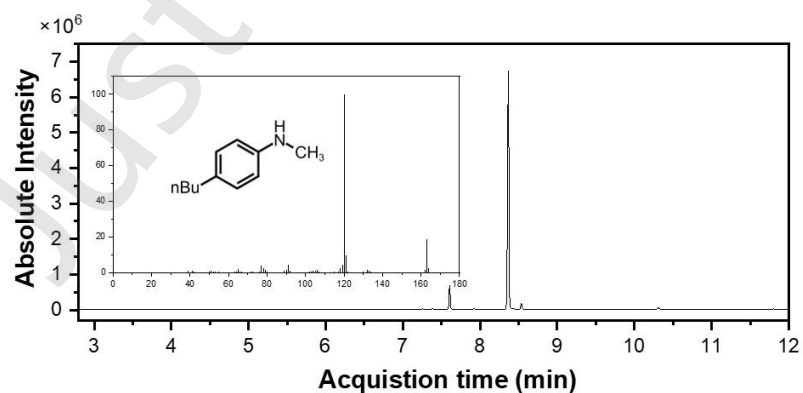


Figure S17. GC-MS spectrum of N-methylation reaction of 4-butylaniline with CO_2/H_2 .

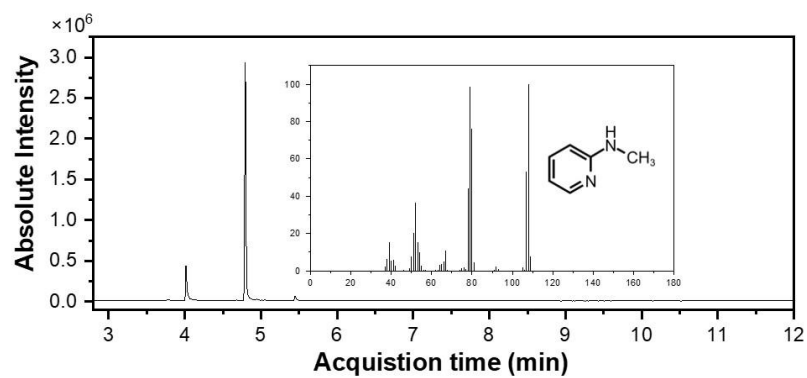


Figure S18. GC-MS spectrum of N-methylation reaction of 2-aminopyridine with CO_2/H_2 .

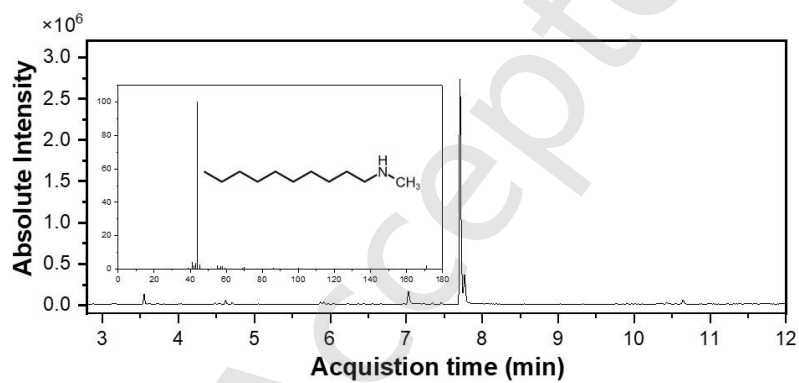


Figure S19. GC-MS spectrum of N-methylation reaction of n-decylamine with CO_2/H_2 .

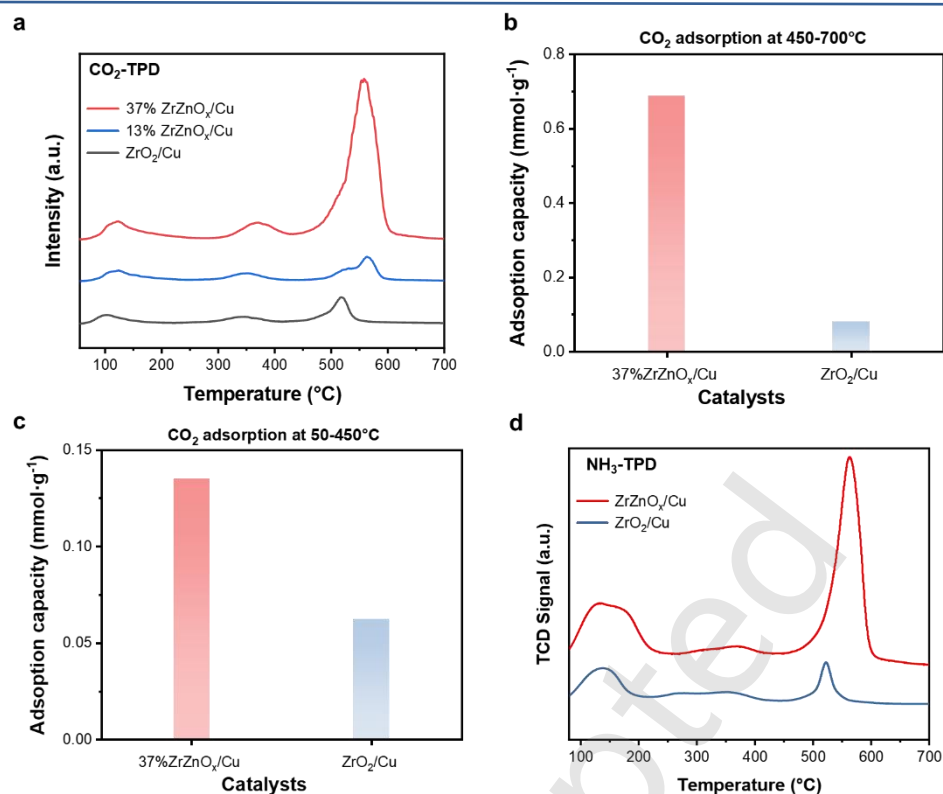


Figure S20. (a) CO₂-TPD profiles of ZrO₂/Cu and ZrZnO_x/Cu catalysts; Adsorption capacity of CO₂-TPD on the ZrO₂/Cu and ZrZnO_x/Cu catalysts at (b) 450-650 °C and (c) 50-450 °C; (d) NH₃-TPD profiles of ZrO₂/Cu and ZrZnO_x/Cu catalysts.

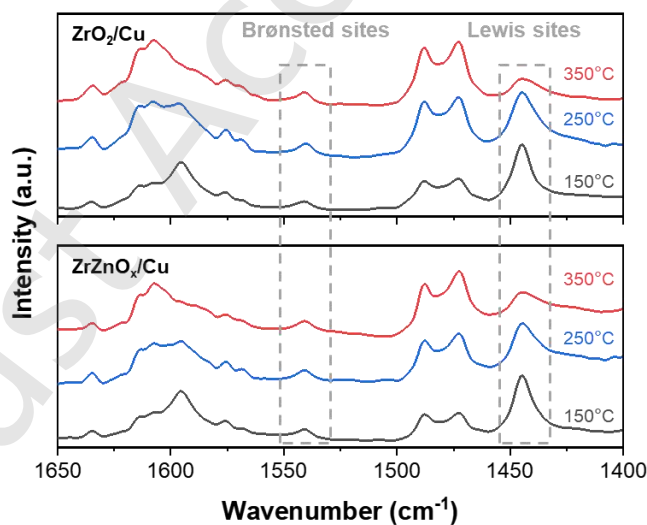


Figure S21. Pyridine-adsorbed FTIR spectra of ZrO₂/Cu and ZrZnO_x/Cu after desorption at 150, 250, and 350 °C.

Table S4. The results of Py-FTIR of ZrO₂/Cu and ZrZnO_x/Cu catalyst

Desorption temperature	150°C		250°C		350°C	
Acid sites (mmol/g)	B	L	B	L	B	L
ZrO ₂ /Cu	0.01033	0.07223	0.00699	0.03600	0.00524	0.01188
ZrZnO _x /Cu	0.01152	0.08381	0.00770	0.03954	0.00612	0.01518

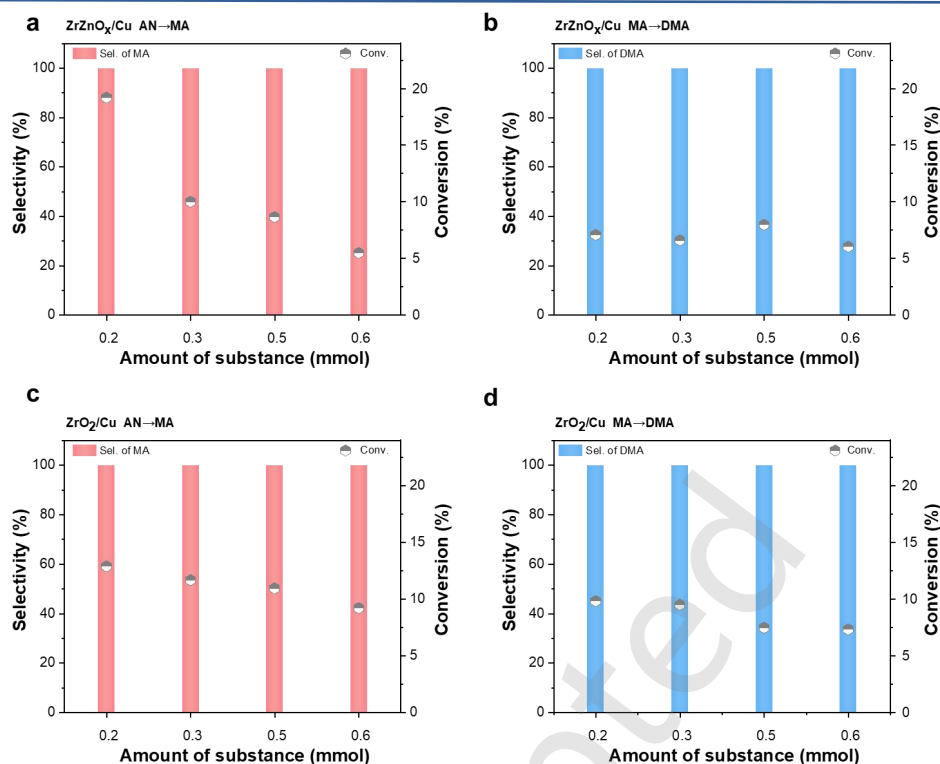


Figure S22. Concentration-dependent reaction performance for the stepwise methylation of aniline over ZrZnO_x/Cu and ZrO₂/Cu catalysts. Reaction conditions: 150 °C, 15 mL n-hexane, and 0.2 mmol m-xylene as the internal standard. **(a)** 50 mg catalyst for AN→MA over ZrZnO_x/Cu; **(b, c, d)** 100 mg catalyst for all other tests

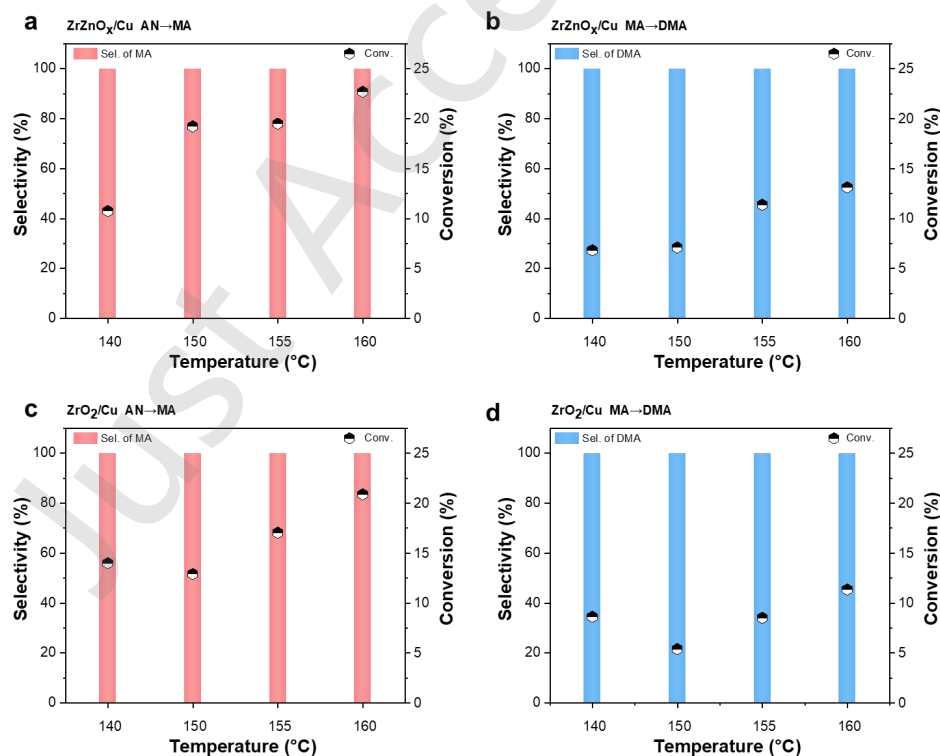


Figure S23. Temperature-dependent reaction performance for the stepwise methylation of aniline over ZrZnO_x/Cu and ZrO₂/Cu catalysts. Reaction conditions: 0.2 mmol AN, 15 mL n-hexane, and 0.2 mmol m-xylene as the internal standard. Catalyst mass details: To ensure the conversion was within a measurable and kinetically controlled range across the entire temperature window, the catalyst mass was adjusted as follows: **(a, b)** AN→MA over ZrZnO_x/Cu, 40 mg at 160 °C, and 50 mg at other temperatures; **(b)** MA→DMA over ZrZnO_x/Cu 100 mg at all temperatures; **(c, d)** 100 mg ZrO₂/Cu.

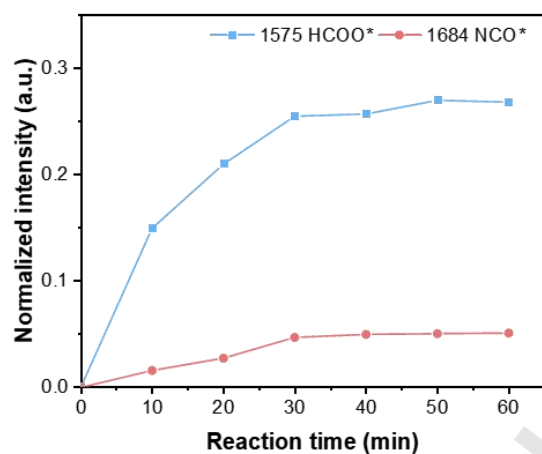


Figure S24. Normalized intensities of representative in situ DRIFTS bands under CO_2/H_2 and aniline co-feeding conditions over ZrZnO_x/Cu .

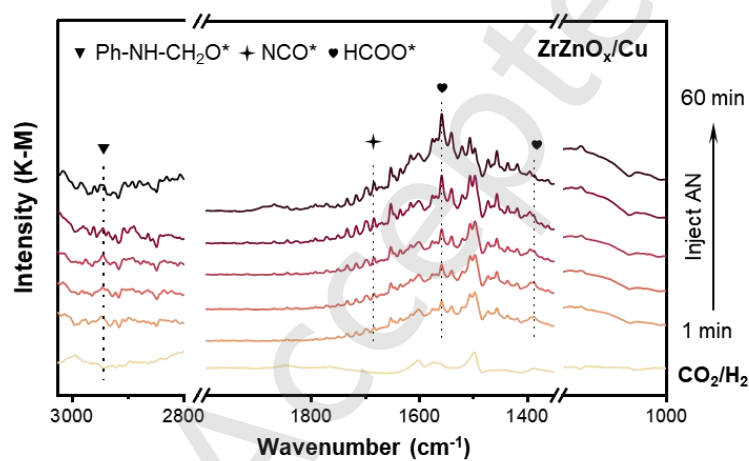


Figure S25. In situ DRIFTS spectra on ZrZnO_x/Cu after CO_2/H_2 introduction followed by switching to AN vapor.

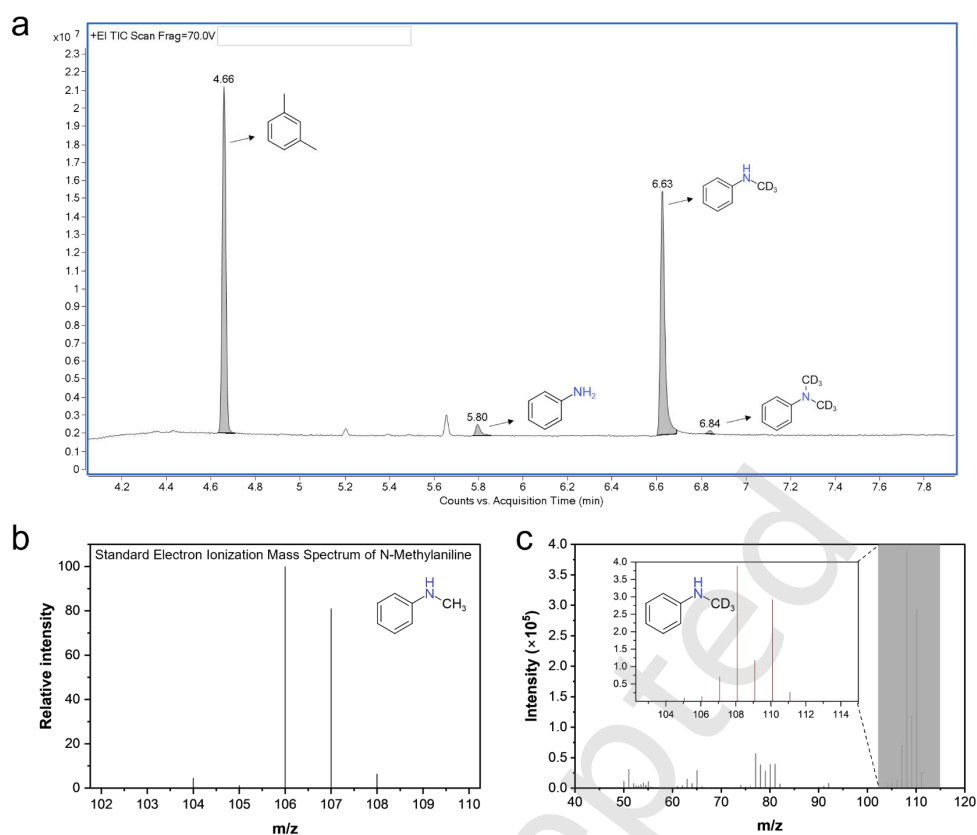


Figure S26. GC-MS analysis of the D₂ isotope-labeling experiment for CO₂-driven N-monomethylation of aniline over ZrZnO_x/Cu. **(a)** Total ion chromatogram (TIC) of the reaction mixture obtained under a CO₂/D₂ atmosphere. **(b)** Standard electron ionization mass spectrum of N-methylaniline from the mass spectral library. **(c)** EI mass spectrum of the monomethylated product obtained from the D₂-labeling experiment. The inset shows an enlarged view of the m/z 104–112 region. Reaction conditions: 100 mg catalyst, 0.2 mmol AN, 15 mL n-hexane, 3.0 MPa D₂/CO₂/N₂, 150 °C, 3 h, 800 rpm, m-xylene as an internal standard.