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# Multi-Scale Assessment of Methanol Synthesis on ZrO2-on-Cu Inverse Catalysts

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## Abstract

**Bridging atomistic insights with reactor-level performance is essential for catalyst evaluation. In this study, a multi-scale framework integrating DFT calculations, microkinetic modeling, and plug-flow reactor simulations was developed for ZrO2-on-Cu inverse catalysts. The model predicts methanol space–time yields of 0.60–0.65 g $g^{-1}$ $h^{-1}$ under industrial conditions. Interface site density emerges as the dominant descriptor controlling productivity, outweighing surface area effects. The approach provides a quantitative link between interface chemistry and macroscopic performance.**

## Keywords

**multi-scale modeling; inverse catalyst; ZrO2/Cu; methanol synthesis; CO2 hydrogenation**

## 1.Introduction

Methanol production from $CO_2$ and low-carbon hydrogen is widely recognized as a promising pathway for reducing carbon emissions while leveraging existing chemical infrastructure [1]. As both an energy carrier and a versatile platform chemical, methanol provides an effective bridge between intermittent renewable power generation and downstream fuels, chemicals, and materials [2]. Despite extensive research efforts, achieving high methanol productivity and selectivity under industrially relevant pressures remains challenging. Methanol formation competes strongly with the reverse water–gas shift (RWGS) reaction, and catalytic performance is highly sensitive to temperature, pressure, and feed composition [3]. Recent reactor-level investigations further demonstrate that transport limitations and operating windows can substantially alter apparent reaction trends, indicating that intrinsic kinetics alone are insufficient to explain observed catalytic behavior under realistic conditions [4]. Copper-based catalysts continue to serve as the industrial benchmark for methanol synthesis, yet their effectiveness in $CO_2$ hydrogenation depends critically on the presence of promoters and metal–oxide interfaces [5]. Among various oxide components, $ZrO_2$ has been consistently shown to enhance $CO_2$ activation and methanol selectivity when combined with Cu [6]. Carefully designed experimental studies that control the extent of Cu–$ZrO_2$ contact reveal that catalytic activity correlates more strongly with interfacial structure than with Cu surface area alone [7]. These observations support a mechanistic picture in which methanol synthesis proceeds through cooperative metal–oxide ensembles rather than isolated metallic Cu sites. At such interfaces, adsorbed intermediates can exchange between metal and oxide domains, modifying reaction pathways and suppressing undesired RWGS activity through interfacial stabilization and altered hydrogenation sequences [8]. Growing recognition of the central role of metal–oxide boundaries has stimulated interest in inverse catalyst architectures, where oxide nanoparticles are dispersed directly onto metallic substrates [9]. This configuration maximizes metal–oxide perimeter length while preserving efficient hydrogen activation on the metal phase. Inverse $ZrO_2$-on-Cu catalysts have been reported to exhibit enhanced methanol selectivity and modified reaction kinetics relative to conventional supported systems, underscoring the importance of interface density and oxide coverage as key structural descriptors [10]. Importantly, recent theoretical and experimental analyses indicate that $CO_2$ hydrogenation on inverse catalysts is governed by ensembles of interfacial sites rather than a single dominant active site, particularly under elevated pressures relevant to industrial operation [11]. This ensemble-based perspective provides a conceptual shift from traditional site-specific descriptions and highlights interface density as a potentially quantifiable and tunable parameter. At the same time, inverse catalysts introduce new challenges for performance evaluation and mechanistic interpretation. The distribution of active sites is inherently heterogeneous, and oxide domains may restructure, partially reduce, or migrate under reaction conditions [12]. Operando studies show that promoters and oxide components can dynamically evolve at high pressures, leading to time-dependent changes in interfacial site populations and catalytic behavior [13]. As a result, structure–activity relationships inferred from ex situ characterization or low-pressure experiments may not remain valid under industrial conditions. In addition, many experimental datasets vary multiple structural parameters simultaneously, complicating efforts to isolate the specific influence of interface density from changes in particle size, dispersion, or surface area [14]. Multiscale modeling offers a powerful framework for addressing these challenges, yet current approaches remain fragmented. Density functional theory and microkinetic modeling are widely applied to elucidate reaction pathways and rate-controlling steps on Cu-based and oxide-modified surfaces. In parallel, reactor-scale models have been developed to describe methanol synthesis under industrial operating conditions [15]. However, most microkinetic models rely on idealized surface representations and simplified site definitions, while reactor simulations often inherit these assumptions without explicitly accounting for interfacial site heterogeneity. Consequently, the connection between atomistic interface chemistry and reactor-level productivity remains largely qualitative, limiting the predictive capability of such models [16]. In this work, a multiscale framework is developed to explicitly bridge atomistic interface chemistry and macroscopic reactor performance for $ZrO_2$-on-Cu inverse catalysts. Density functional theory calculations are combined with interface-resolved microkinetic modeling and plug-flow reactor simulations under industrially relevant conditions. Interfacial site density is introduced as an explicit model parameter, enabling its impact on methanol space–time yield to be quantified independently of surface area effects. By propagating interface-specific energetics across length scales, this approach establishes a direct and quantitative link between metal–oxide ensemble chemistry and reactor-level performance, providing a rational basis for evaluating and optimizing inverse catalyst designs using industrially meaningful criteria.

## 2.Materials and Methods

### 2.1 Sample and System Description

This study examines $ZrO_2$-on-Cu inverse catalyst systems for $CO_2$ hydrogenation to methanol. A set of model catalysts with different $ZrO_2$ coverages was considered to represent a range of metal–oxide interface densities. The catalytic surface was described using Cu facets partially covered by $ZrO_2$ clusters, consistent with inverse structures reported in experimental studies. Reaction conditions were selected to match typical industrial methanol synthesis, including pressures of 50–80 bar and temperatures between 220 and 260 °C. The feed composition was based on $CO_2/H_2$ ratios commonly used in practical operation. These conditions allow kinetic and reactor behavior to be examined under realistic operating environments.

### 2.2 Experimental Design and Control Cases

To clarify the role of metal–oxide interfaces, inverse $ZrO_2$-on-Cu systems were compared with reference surfaces lacking oxide decoration. Bare Cu surfaces and configurations with limited interface exposure were used as control cases. The inverse catalysts formed the main study group, while the reference systems served as benchmarks. This comparison makes it possible to separate interface effects from changes in total surface area. The design ensures that differences in activity and selectivity can be attributed primarily to variations in interfacial site density.

### 2.3 Measurement Methods and Quality Control

Elementary reaction energetics were obtained from density functional theory calculations using periodic slab models. Plane-wave cutoffs, slab thickness, and k-point meshes were tested to ensure numerical convergence. Adsorption energies and transition-state barriers were evaluated using consistent computational settings. Kinetic parameters were derived from the same energetic dataset to maintain internal consistency. Reactor calculations were based on steady-state mass and energy balances. Numerical stability was verified by checking the independence of results from initial conditions and grid resolution.

### 2.4 Data Processing and Model Formulation

Reaction rates were described using an elementary-step kinetic scheme. The net rate of methanol formation was calculated as

$$r_{MeOH}=\sum_i \nu_i k_i \prod_j \theta_j$$

Where $k_i$ represents the rate constant of step i, $\theta_j$ denotes surface coverages, and$\nu_i$ is the stoichiometric coefficient. Reactor performance was evaluated using a plug-flow model. The molar balance for species k along the catalyst bed was written as

$$\frac{dF_k}{dW}=r_k$$

With $F_k$ as the molar flow rate and W as the catalyst mass. Methanol space–time yield was calculated from the outlet methanol flow normalized by catalyst mass. Data analysis focused on the effect of interface site density under fixed operating conditions.

### 2.5 Model Integration and Sensitivity Analysis

Atomistic calculations, kinetic modeling, and reactor simulations were linked in a stepwise manner. Interfacial site density was introduced as an explicit parameter connecting surface structure with overall reaction rates. Sensitivity analysis was carried out by varying key kinetic parameters and site densities independently. The resulting changes in methanol space–time yield and $CO_2$ conversion were examined. This approach allows identification of the factors that most strongly influence reactor performance.

## 3.Results and Discussion

### 3.1 Interface energetics and the origin of activity

The calculated energetics show that $CO_2$ activation is favored at $ZrO_2$–Cu boundary sites, while hydrogenation steps remain kinetically accessible on adjacent Cu domains. This behavior supports a bifunctional reaction picture in which oxygen-containing intermediates are stabilized near oxide-associated sites rather than on extended Cu terraces. In this system, effective methanol formation requires efficient transfer of intermediates across the metal–oxide boundary, making perimeter availability more important than nominal Cu surface area once Cu dispersion is sufficiently high. Similar conclusions have been drawn in recent studies showing that catalytic performance can be improved by enhancing hydrogen delivery to oxide-related sites, even without increasing overall metal exposure [17]. Fig.1. Nanoscale hydrogen-delivery concept and the associated performance gains in $CO_2$-to-methanol catalysis.

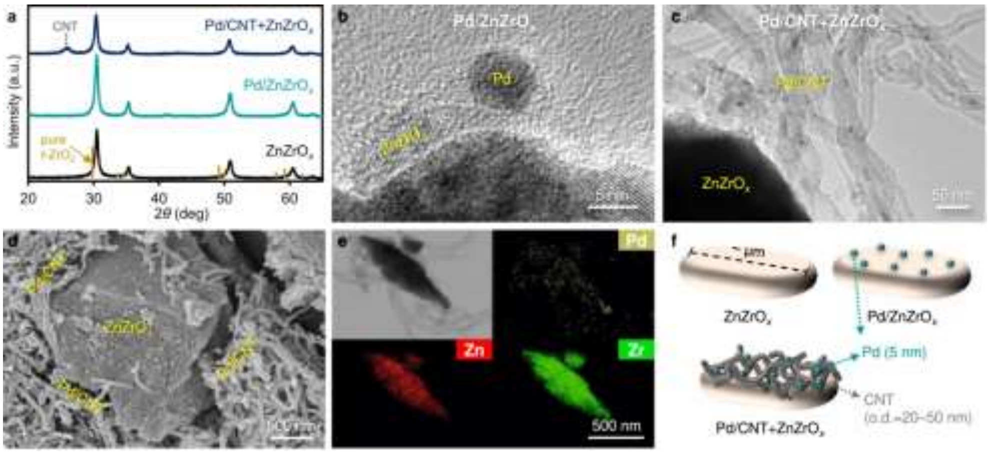

**Figure 1 Illustration of hydrogen transport at metal–oxide interfaces and its effect on methanol formation during $CO_2$ hydrogenation.**

## 3.2 Microkinetic sensitivity and the role of interface site density

Microkinetic analysis shows that the methanol formation rate responds most strongly to the number of available interfacial ensembles, defined as oxide-related activation sites located next to Cu hydrogenation sites. When interface site density is increased while intrinsic barriers are kept constant, the model predicts a near-linear increase in methanol production until transport and equilibrium effects limit further gains. In contrast, increasing Cu surface area without expanding the boundary length leads to smaller improvements, because the rate-limiting steps still require cooperation between oxide and metal sites. This behavior is consistent with recent efforts to distinguish perimeter sites from bulk-like metal sites when interpreting activity trends under $CO_2$-rich conditions, where RWGS competition and water effects often obscure simple surface-area correlations [18].

## 3.3 Reactor-level performance and comparison with literature data

When the kinetic description is embedded into a plug-flow reactor model under industrially relevant pressure and temperature, the predicted methanol space–time yield reaches 0.60–0.65 g $g^{-1}$ $h^{-1}$. The axial profiles show that productivity is governed by the balance between

$CO_2$ conversion near the reactor inlet and composition shifts caused by product accumulation downstream. This explains why high intrinsic reaction rates measured under differential conditions do not always translate into proportional gains at the reactor scale. Comparable trends are reported for Cu-doped ZnO–$ZrO_2$ catalysts, where variations in composition and temperature shift the balance between conversion and selectivity rather than producing monotonic improvements in both metrics [19]. Fig.2. $CO_2$ conversion and $CH_3OH$ selectivity trends across Cu-doped ZnO–$ZrO_2$ solid-solution catalysts, illustrating the conversion–selectivity trade-off with composition and temperature.

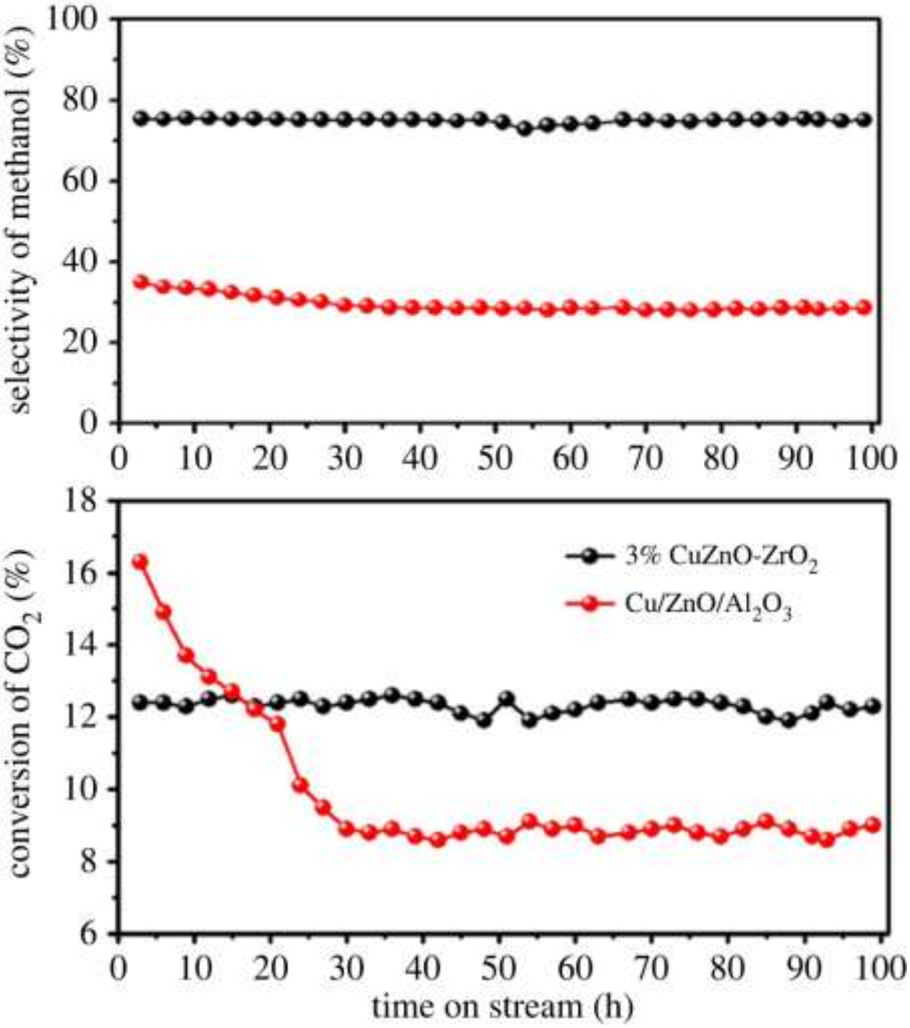

**Figure 2 $CO_2$ conversion and methanol selectivity measured at different catalyst compositions and temperatures for Cu-doped ZnO–ZrO2 catalysts.**

### 3.4 Implications for catalyst design and remaining limitations

By linking atomistic energetics with reactor-scale performance, the analysis identifies interface site density as a key factor controlling methanol productivity in inverse $ZrO_2$-on-Cu systems. The results show that productivity depends on the number of cooperative metal–oxide ensembles capable of sustaining the full $CO_2$ activation and hydrogenation sequence, rather than on surface area alone. Once these ensembles approach saturation, further improvements require better delivery of hydrogen or intermediates to the boundary, or mitigation of deactivation effects associated with water accumulation [20]. Remaining uncertainties mainly arise from changes in interface structure under reaction conditions, coverage-dependent kinetic parameters not fully captured by simplified surface models, and potential gradients within catalyst pellets at larger scales. These factors point to the need for future studies that combine operando site characterization with reactor-scale validation.

## 4.Conclusion

This study links metal–oxide interface chemistry with reactor-level methanol productivity for $ZrO_2$-on-Cu inverse catalysts through combined atomistic, kinetic, and reactor analyses. The results show that methanol formation is mainly controlled by the density of cooperative interface sites, rather than by total metal surface area. This finding explains why inverse catalyst architectures can outperform conventional Cu-based systems under industrial conditions. By explicitly relating interface site density to space–time yield, the analysis shows how boundary sites govern both reaction pathways and overall reactor performance. The approach offers a practical way to assess catalyst designs using performance-related descriptors instead of surface-area metrics alone. Several limitations remain, including simplified surface models, fixed kinetic parameters, and the absence of long-term structural changes under reaction conditions. Further studies that combine operando measurements with scale-dependent validation are needed to improve predictive accuracy and to support the design of methanol synthesis catalysts for industrial application.

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