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Defect-Driven CO_2 Activation at Oxygen-Deficient ZrO_2–Cu Interfaces

Claire Moreau[1], Julien Lefèvre[2], Antoine Dubois[3]*

Department of Chemistry, École Normale Supérieure, Université PSL, 75005 Paris, France

***Corresponding author:** antoine.dubois@univ-psl.fr

Abstract

Defects in oxide components often play a decisive role in catalytic activity. In this study, oxygen vacancies were systematically introduced into ZrO2 clusters supported on Cu to evaluate their effect on CO2 hydrogenation. Vacancy formation enhances local charge localization and strengthens CO2 adsorption by up to 0.44 eV. Microkinetic analysis shows that moderate vacancy concentrations (3–6%) maximize methanol selectivity, whereas higher defect densities favor CO formation. These results demonstrate how controlled defect engineering can fine-tune inverse catalyst performance.

Keywords

oxygen vacancies; defect engineering; ZrO2/Cu; CO2 activation; methanol synthesis

1.Introduction

Carbon dioxide hydrogenation to methanol represents a strategically important route for carbon utilization, as methanol serves both as a liquid energy carrier and as a key C1 intermediate for fuels and chemical synthesis [1]. Although Cu–ZnO–Al_2O_3 catalysts have been applied industrially for decades, maintaining high catalytic activity and methanol selectivity under CO_2-rich reaction conditions remains challenging. This difficulty primarily stems from the limited intrinsic ability of metallic Cu to activate CO_2, as well as from the strong sensitivity of C–O bond transformation to the local electronic environment at metal–oxide interfaces [2]. Increasing evidence indicates that catalyst performance is governed not only by bulk composition, but also by the atomic-scale structure and chemical nature of interfacial sites adjacent to Cu surfaces, where cooperative interactions between metal and oxide phases occur [3]. Zirconia has emerged as an effective oxide component for Cu-based methanol synthesis catalysts because ZrO_2 can stabilize oxygenated reaction intermediates while preserving efficient hydrogen activation on metallic Cu. Experimental observations combined with density functional theory calculations consistently show that Cu–ZrO_2 interfaces enhance CO_2 conversion compared with oxide-free Cu surfaces [4]. Importantly, recent theoretical studies demonstrate that methanol formation on ZrO_2-modified Cu does not originate from a single dominant active site, but rather arises from the collective contribution of multiple

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interfacial configurations with distinct energetic characteristics [5]. This ensemble-based description highlights the critical role of interfacial heterogeneity and suggests that catalytic behavior cannot be accurately captured by simplified single-site models. In parallel, inverse catalyst architectures, in which ZrO_2 clusters are supported directly on metallic Cu, have attracted growing attention because they expose a high density of perimeter sites with tunable electronic properties and flexible structural motifs [6,7]. At the atomic scale, a key factor governing the reactivity of ZrO_2–Cu interfaces is the presence of oxygen vacancies within the oxide phase. Oxygen-deficient ZrO_2 can induce localized electronic states, modify charge transfer between ZrO_2 and Cu, and generate coordinatively unsaturated Zr centers. These features enhance CO_2 adsorption and facilitate the formation of surface formate and methoxy species, which are widely proposed as key intermediates in methanol synthesis [8]. At the same time, vacancy effects are not uniformly beneficial. Excessive defect densities may overly stabilize oxygenated intermediates or promote C–O bond cleavage, thereby favoring CO formation through the reverse water–gas shift pathway. Oxygen vacancies therefore act as regulators of product selectivity rather than as simple activity enhancers, and their influence depends sensitively on concentration and local coordination environment [9,10]. Despite extensive experimental and theoretical investigation, several limitations remain in current studies of defect-mediated CO_2 hydrogenation on ZrO_2–Cu catalysts. In many experimental works, oxygen vacancy concentrations are inferred indirectly from reduction treatments or ex situ characterization, while their population, distribution, and stability under reaction conditions are rarely quantified explicitly. On the theoretical side, most models consider a limited number of idealized vacancy configurations on small oxide clusters or flat surfaces, which does not reflect the structural diversity of realistic inverse catalysts, where ZrO_2 domains vary in size, morphology, and defect distribution [11]. Moreover, selectivity conclusions are often drawn from adsorption energies or isolated reaction barriers, even though the final product distribution is determined by the coupled kinetics of multiple competing elementary steps across different interfacial sites. In this context, the present study provides a systematic investigation of oxygen-deficient ZrO_2 clusters supported on Cu, with explicit control over vacancy concentration as a continuous design parameter. Density functional theory calculations are combined with electronic structure analysis to elucidate how vacancy-induced charge localization influences CO_2 binding and intermediate stabilization at the ZrO_2–Cu interface. These insights are further integrated into microkinetic modeling to evaluate how changes in vacancy concentration propagate through the reaction

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network and alter the competition between methanol synthesis and CO formation. By establishing a quantitative relationship between oxygen vacancy concentration, interfacial electronic structure, and product selectivity, this work advances the mechanistic understanding of defect-controlled catalysis and provides practical guidance for the rational design of inverse ZrO_2/Cu catalysts optimized for selective CO_2 hydrogenation to methanol.

2.Materials and Methods

2.1 Sample and System Description

The studied systems consisted of ZrO_2 clusters supported on Cu surfaces, used to model inverse oxide–metal interfaces relevant to CO_2 hydrogenation. ZrO_2 clusters containing 6–12 Zr atoms were constructed to represent nanoscale oxide domains. Oxygen vacancies were introduced by removing lattice oxygen atoms, resulting in vacancy concentrations between 0% and 12%. The Cu support was described by a periodic Cu(111) slab, which is commonly reported as a stable surface under reaction conditions. All structures were fully relaxed to obtain stable interfacial geometries, with attention given to Zr coordination environments, Cu–O bonding, and the spatial location of vacancies relative to interfacial sites.

2.2 Experimental Design and Control Systems

A comparative framework was adopted to evaluate the influence of oxygen vacancies on CO_2 activation and reaction pathways. Stoichiometric ZrO_2/Cu interfaces were used as reference systems, while defect-containing interfaces formed the test set. Vacancy concentration was increased stepwise to examine its effect on adsorption strength and reaction energetics. For each vacancy level, several vacancy arrangements were considered to reduce configuration-dependent bias. Pure Cu(111) surfaces and isolated ZrO_2 clusters were also examined as control models, allowing separation of interfacial effects from those intrinsic to the metal or oxide phases.

2.3 Measurement Methods and Quality Control

Electronic structure calculations were carried out using density functional theory under periodic boundary conditions. Structural optimizations and total energy calculations employed a generalized gradient approximation with dispersion corrections to account for weak interactions. Adsorption energies were determined after full relaxation of all atoms. Transition states were identified using constrained optimization and verified by vibrational analysis showing a single imaginary frequency. Convergence tests were performed for plane-

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wave cutoff energy, k-point sampling, and slab thickness. Charge distribution was analyzed using Bader charge analysis. The same computational settings were applied to all systems to maintain internal consistency.

2.4 Data Processing and Model Formulation

Adsorption energies were calculated using

$$E_{ads}=E_{surf+mol}-E_{surf}-E_{mol},$$

where $E_{surf+mol}$ is the total energy of the adsorption system, and E_{surf} and E_{mol} are the energies of the clean surface and the gas-phase molecule, respectively. Rate constants for elementary reactions were estimated using transition state theory:

$$k=\frac{k_B T}{h}\exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right),$$

where $\Delta G^{\ddagger}$ denotes the Gibbs free energy barrier. These values were used as inputs for kinetic analysis.

2.5 Microkinetic Analysis and Selectivity Evaluation

A microkinetic model was developed to describe adsorption, surface reactions, and desorption steps involved in CO_2 hydrogenation and the reverse water–gas shift reaction. Steady-state rate equations were solved numerically to obtain formation rates of methanol and CO. Methanol selectivity was defined as

$$S_{MeOH}=\frac{r_{MeOH}}{r_{MeOH}+r_{CO}},$$

where r_{MeOH} and r_{CO} are the respective production rates. Sensitivity analysis was performed to identify key elementary steps controlling selectivity and to evaluate how changes in vacancy concentration affect reaction pathways.

3.Results and Discussion

3.1 Defect-Controlled Charge Redistribution and CO_2 Adsorption

The introduction of oxygen vacancies at ZrO_2–Cu interfaces resulted in clear changes in local charge distribution. Excess electrons accumulated near under-coordinated Zr atoms adjacent to vacancy sites, increasing the polarization of adsorbed CO_2 molecules. As a result, CO_2 adopted a bent adsorption geometry at interfacial perimeter sites, indicating activation of the linear molecule. The calculated adsorption energies showed that CO_2 binding was strengthened by up to 0.44 eV compared with stoichiometric interfaces. Similar behavior has

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been reported for Cu–Zr-based catalysts, where interfacial oxygen species and localized charge play a key role in stabilizing oxygenate intermediates [12]. Recent studies further demonstrate that Cu–O–Zr motifs promote CO_2 activation more effectively than metallic Cu surfaces alone, supporting the importance of defect-modified oxide–metal interfaces in CO_2 hydrogenation chemistry.

3.2 Preference for Methanol Formation at Moderate Vacancy Concentrations

At moderate oxygen vacancy concentrations (3–6%), the ZrO_2–Cu interface maintained a balanced interaction with reaction intermediates. CO_2 activation and early hydrogenation steps were facilitated, while subsequent hydrogenation reactions remained kinetically accessible. In this regime, vacancy-adjacent Zr sites promoted the formation of oxygenated intermediates, whereas nearby Cu atoms provided active hydrogen species. This combination supported continuous hydrogenation toward methoxy and methanol products without excessive accumulation of strongly bound surface species. Comparable trends have been observed in Cu–ZrO_x catalysts, where methanol selectivity is highest when interfacial sites stabilize intermediates sufficiently for reaction but do not hinder turnover. These observations indicate that selectivity depends on achieving balanced adsorption rather than maximizing defect density [13].

3.3 Microkinetic Origin of the Methanol-to-CO Selectivity Shift

Microkinetic analysis revealed a clear transition in product selectivity as vacancy concentration increased. Methanol selectivity reached its maximum within the 3–6% vacancy range, whereas higher defect levels increasingly favored CO formation. This shift arises from changes in surface coverage and rate competition between hydrogenation and reverse water–gas shift pathways. At high vacancy densities, oxygenated intermediates bind more strongly, which slows hydrogenation and increases the relative contribution of CO-producing routes. Similar selectivity shifts have been reported for Cu–ZrO_2 systems with high oxide reducibility, where enhanced CO_2 activation leads to increased CO production when hydrogenation becomes less competitive [14]. These results confirm that vacancy concentration controls not only activity but also the dominant reaction pathway.

3.4 Comparison with Literature and Implications for Catalyst Design

The vacancy-dependent optimum observed here follows a general pattern reported for inverse Cu–oxide catalysts, where catalytic performance peaks at intermediate oxide or defect

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levels. Previous experimental studies show that methanol productivity depends on a balance between oxide-derived interfacial sites and available Cu surface area, rather than on oxide content alone (Fig.2). In addition, recent reports on inverse Zr–Cu catalysts demonstrate that well-dispersed ZrO_x domains enhance methanol synthesis only when excessive reduction is avoided (Fig.1). The present results provide a mechanistic explanation for these observations by linking vacancy concentration to both adsorption strength and kinetic pathway selection. Together, the comparison indicates that oxygen vacancies should be introduced in a controlled manner to enhance CO_2 activation while preserving efficient hydrogenation, offering a practical guideline for designing selective ZrO_2/Cu inverse catalysts [15].

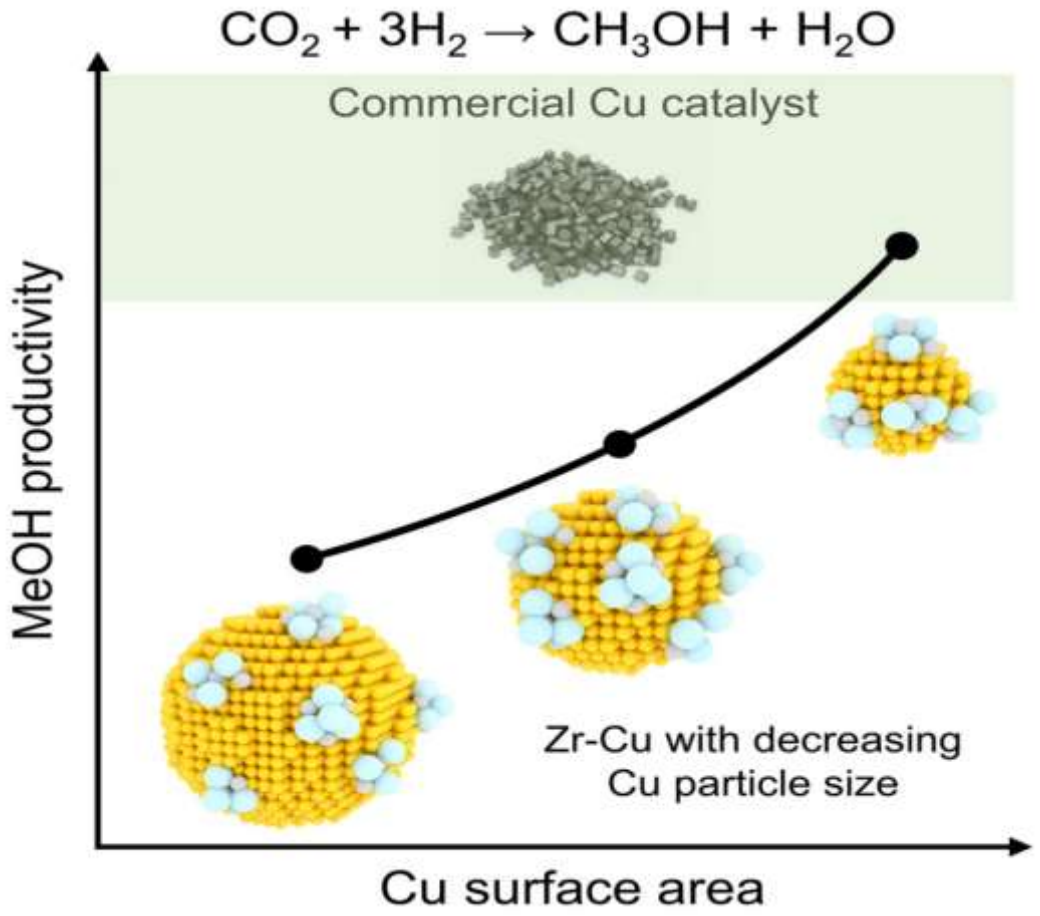

Figure 1 Schematic showing the effect of Cu surface availability and ZrO_x dispersion on methanol productivity in inverse Zr–Cu catalysts during CO2 hydrogenation.

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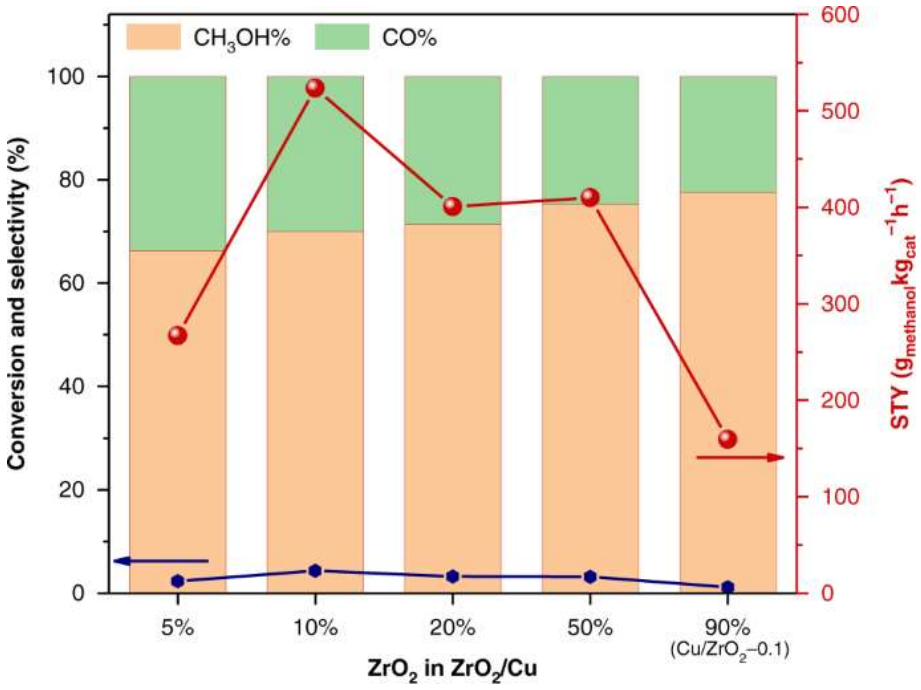

Figure 2 Variation of methanol selectivity and space–time yield with ZrO2 loading in inverse ZrO2/Cu catalysts, showing a maximum at intermediate oxide content.

4. Conclusion

Oxygen vacancy concentration at ZrO_2–Cu interfaces strongly influences CO_2 activation and product distribution during CO_2 hydrogenation. Interfaces with a moderate number of vacancies show enhanced charge redistribution and stronger CO_2 adsorption, which favors the formation and further hydrogenation of oxygenated intermediates toward methanol. When vacancy density becomes high, CO formation is promoted as reaction flux shifts toward reverse water–gas shift pathways. These results clarify why inverse ZrO_2/Cu catalysts often exhibit an intermediate optimum in methanol selectivity and show that vacancy density can be used as a controllable parameter in catalyst design. From an application standpoint, the findings indicate that careful control of interfacial defects can improve methanol selectivity under CO_2-rich conditions. The analysis is based on idealized interface structures and steady-state kinetic modeling, and additional experimental studies under realistic reaction conditions are needed to evaluate catalyst stability and practical performance.

References

[1] Patil, T., Naji, A., Mondal, U., Pandey, I., Unnarkat, A., & Dharaskar, S. (2024). Sustainable methanol production from carbon dioxide: advances, challenges, and future prospects. Environmental Science and Pollution Research, 31(32), 44608-44648.

ISSN: 3008-1394

[2] Peng, H., Dong, N., Liao, Y., Tang, Y., & Hu, X. (2024). Real-Time Turbidity Monitoring Using Machine Learning and Environmental Parameter Integration for Scalable Water Quality Management. Journal of Theory and Practice in Engineering and Technology, 1(4), 29-36.

[3] Bhalothia, D., Beniwal, A., Gurjar, H., Shekhawat, K., Bagaria, A., & Chen, T. Y. (2025). Surface and interface engineering of noble metal heterostructures for superior oRR performance: Unlocking ultralow loading and maximum catalyst utilization. Small, 21(44), e06018.

[4] Zambaldi, P., Haug, L., Penner, S., & Klötzer, B. (2022). Dry reforming of methane on NiCu and NiPd model systems: Optimization of carbon chemistry. Catalysts, 12(3), 311.

[5] Yang, Z., Kumari, S., Alexandrova, A. N., & Sautet, P. (2025). Catalytic Activity of an Ensemble of Sites for CO2 Hydrogenation to Methanol on a ZrO2-on-Cu Inverse Catalyst. Journal of the American Chemical Society, 147(18), 15294-15306.

[6] Beg, M. B., Ali, L., & Altarawneh, M. (2025). Investigating niobium oxide-based materials: Synthesis, characterization, and applications in heterogeneous catalysis. Catalysis Reviews, 1-90.

[7] Xu, K., Xu, X., Wu, H., & Sun, R. (2024). Venturi Aeration Systems Design and Performance Evaluation in High Density Aquaculture.

[8] Hansen, C., Zhou, W., & Copéret, C. (2025). The Universal Role of Gallium in Promoting Methanol Formation across CO2 Hydrogenation Catalysts. Accounts of Chemical Research, 58(22), 3392-3401.

[9] Xu, K., Xu, X., Wu, H., Sun, R., & Hong, Y. (2023). Ozonation and Filtration System for Sustainable Treatment of Aquaculture Wastewater in Taizhou City. Innovations in Applied Engineering and Technology, 1-7.

[10] Ciftyurek, E., Li, Z., & Schierbaum, K. (2022). Adsorbed oxygen ions and oxygen vacancies: their concentration and distribution in metal oxide chemical sensors and influencing role in sensitivity and sensing mechanisms. Sensors, 23(1), 29.

[11] Wang, Y., Wang, Y., Yin, X., Arias, R., & Chen, J. (2026). Research on Dynamic Assessment of Glucose-Lipid Metabolism and Personalized Drug Response Prediction Based on Wearable Multimodal Sensing.

[12] Pinheiro, M. G., de Souza, E. F., Chagas, L. H., Zonetti, P. C., Gonzalez, G. G., Huaman, N. R., ... & Appel, L. G. (2024). The role of oxygen vacancies and Zn in isobutene synthesis from ethanol employing Zn, Zr-based catalysts. Catalysis Science & Technology, 14(10), 2794-2805.

[13] Wang, C., & Chakrapani, V. (2023). Photocatalytic generation of reactive oxygen species on Fe and Mn oxide minerals: mechanistic pathways and influence of semiconducting properties. The Journal of Physical Chemistry C, 127(48), 23189-23198.

ISSN: 3008-1394

[14] Rossi, M. A., Rasteiro, L. F., Vieira, L. H., Fraga, M. A., Assaf, J. M., & Assaf, E. M. (2023). Investigation of in promotion on Cu/ZrO2 catalysts and application in CO2 hydrogenation to methanol. Catalysis Letters, 153(9), 2728-2744.

[15] Wang, C., & Chakrapani, V. (2023). Environmental Factors Controlling the Electronic Properties and Oxidative Activities of Birnessite Minerals. ACS Earth and Space Chemistry, 7(4), 774-787.