Frontiers in Chemistry, Materials and Catalysis Volume 3 Issue 1, 2026
ISSN: 3079-9341

Statistical Modeling of Active Site Distributions on ZrO2-Decorated Copper

Kenji Yamamoto[1], Hiroshi Tanaka[2], Yuki Sato[3]*

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

***Corresponding author:** y.sato@u-tokyo.ac.jp

Abstract

Inverse catalysts exhibit significant site heterogeneity that challenges traditional single-site descriptions. In this study, a statistical model was developed to describe the distribution of active sites at ZrO2–Cu interfaces using DFT-derived energetics. Five dominant site classes were identified and weighted according to their thermodynamic stability. Ensemble-averaged microkinetic simulations show that interfacial Zr–O–Cu motifs contribute over 65% of the methanol formation rate, despite occupying less than 30% of the surface area. The ensemble model improves agreement with experimentally reported turnover frequencies compared to single-site approximations. This work highlights the necessity of statistical treatments for realistic modeling of inverse catalysts.

Keywords

site heterogeneity; statistical modeling; inverse catalyst; ZrO2/Cu; methanol synthesis

1.Introduction

The catalytic hydrogenation of carbon dioxide (CO_2) to methanol represents a central pathway for sustainable chemical production and carbon utilization, as it enables both greenhouse gas mitigation and the storage of renewable energy in liquid fuels [1. Industrially, copper-based catalysts remain the benchmark system for this reaction; however, their practical application is constrained by limited thermal stability, structural degradation under reaction conditions, and sensitivity to dynamic surface restructuring [2]. These limitations have motivated extensive efforts to develop alternative catalyst architectures that can enhance activity while maintaining long-term stability. Among the proposed strategies, inverse catalyst designs—where oxide species are dispersed on a metal surface—have emerged as a particularly effective approach [3]. In this configuration, ZrO_2-supported copper surfaces (ZrO_2/Cu) exhibit markedly higher methanol synthesis rates than conventional Cu-based catalysts, highlighting the critical role of metal–oxide interfaces in promoting catalytic performance [4]. Both spectroscopic measurements and kinetic experiments indicate that interfacial sites facilitate cooperative activation of CO_2 and hydrogen, thereby lowering key reaction barriers [5]. Recent theoretical work further demonstrates that methanol formation on ZrO_2/Cu does not proceed on a single dominant site, but instead arises from a collective contribution of multiple interfacial configurations with distinct energetic characteristics [6]. This ensemble-based perspective challenges the traditional assumption of a uniform active center and underscores the complexity of real inverse catalyst surfaces. Despite these advances, the theoretical description of ZrO_2/Cu catalysts remains incomplete. Most density functional theory (DFT) studies adopt simplified surface models that assume a single, well-defined interfacial structure to represent catalytic behavior [7]. Such models typically focus on the most stable geometry identified at zero temperature and treat it as the sole contributor to reaction kinetics. In practice, however, working catalyst surfaces are structurally heterogeneous, containing a distribution of oxide cluster sizes, coordination environments, step edges, and defect sites that evolve under reaction conditions [8]. Neglecting this diversity leads to systematic inaccuracies in predicted reaction energetics and rate constants, particularly when less abundant but highly active sites dominate overall turnover [9]. Experimental observations consistently reveal the coexistence of multiple active motifs, yet these are rarely incorporated into theoretical rate models [10]. Growing evidence across heterogeneous catalysis indicates that statistically rare configurations can exert a disproportionate influence on macroscopic reaction rates when they offer substantially lower activation barriers [11]. For inverse oxide–metal systems, this effect is further amplified by the dynamic nature of oxide clusters, which can restructure, migrate, or change oxidation state during CO_2 hydrogenation [12]. Static DFT models are inherently unable to capture the probabilistic occupation of these configurations or their temperature-dependent population under operating conditions [13]. As a result, a significant gap persists between conventional theoretical predictions and the experimentally observed performance of complex interfacial catalysts [14]. In this work, a statistical framework is developed to bridge this gap for the ZrO_2/Cu inverse catalyst. The approach integrates DFT-derived reaction energetics with Boltzmann statistics to account explicitly for the distribution of accessible interfacial structures under realistic conditions. Multiple distinct site types at the ZrO_2–Cu interface are identified and characterized, and their relative contributions to methanol synthesis are evaluated through ensemble-averaged kinetic simulations. By linking structural heterogeneity to catalytic output in a quantitative manner, this study provides a physically grounded description of how interfacial complexity governs reactivity. The proposed methodology offers a generalizable route for improving theoretical predictions of heterogeneous catalysts where activity emerges from an ensemble of dynamically populated sites rather than a single idealized structure.

2.Materials and Methods

2.1 Description of Computational Samples

A set of surface models represented the catalyst. The dataset contained 20 different structures of ZrO_2 clusters on a Cu(111) surface. These structures showed different orientations and boundaries. The copper base was a four-layer slab with a p(4×4) unit cell. A vacuum space of 15 Å separated the vertical layers. This sample size covers the main structure differences found in experiments. All models were relaxed to find stable states.

2.2 Experimental Design and Controls

Two methods were compared to test the effect of site variety. The first method (Ensemble Model) used five different site classes from the dataset. These classes ranged from stable to less stable structures. The second method (Single-Site Model) used only the most stable structure. Comparing these two methods shows the error caused by assuming a uniform surface. The energy stability of each site decided its weight in the model.

2.3 Measurement and Quality Control

DFT calculations obtained the energies using the VASP code. The PBE functional treated the electron interactions. The cutoff energy was 450 eV. A3×3×1 grid sampled the Brillouin zone. The convergence limit was 10-5 eV. Forces were relaxed to below 0.02 eV/Å. The CI-NEB method found the transition states. Frequency analysis checked that each transition state had exactly one imaginary mode.

2.4 Data Processing and Formulas

Boltzmann statistics found the population of each active site. This method assumes thermodynamic equilibrium. Eq. (1) calculates the probability (Pi) of finding a specific site i:

$$P_i = \frac{\exp\left(-E_i/k_B T\right)}{\sum_j \exp\left(-E_j/k_B T\right)}$$

Where Ei is the site energy and T is the temperature. Eq. (2) calculates the total rate (r_{total}) as the weighted average:

$$r_{total} = \sum_i P_i \times r_i$$

This formula combines the rates of both common and rare sites.

2.5 Statistical Analysis and Validation

The model results were compared with experimental turnover frequencies (TOF). The calculated rates matched literature values for ZrO_2/Cu catalysts at 523 K. Sensitivity analysis checked how energy errors changed the site distribution. Degree of Rate Control (DRC) analysis found the most important site class. The model was valid because the predicted TOF matched the experimental data within one order of magnitude.

3.Results and Discussion

3.1 Identification of Active Site Classes

The DFT calculations scanned the surface energy for ZrO_2 clusters on Cu(111). The search found five different classes of interface sites. These classes have different Zr coordination numbers. Class A is the most stable structure. In this structure, the cluster lies flat on the surface. Class B and C are metastable structures. Their energies are 0.15 to 0.30 eV higher than Class A. These sites have under-coordinated Zr atoms at the edges. The electronic analysis shows that Class B sites have a higher d-band center. This result suggests that the most common sites are not always the most active ones [15].

3.2 Thermodynamic Distribution of Sites

Boltzmann statistics calculated the site populations at 523 K. The results show that the surface structure depends on temperature. Fig. 1 shows the formation energies and stability of the different models. As shown in the figure, Class A is the main structure at low temperatures. However, the number of metastable Class B and C sites increases as temperature rises. At reaction conditions, these active sites cover about 25% of the interface area. This thermal effect lets the catalyst use reaction paths that are not available to the ground state. This finding shows the need to include thermal sampling in the model [16,17].

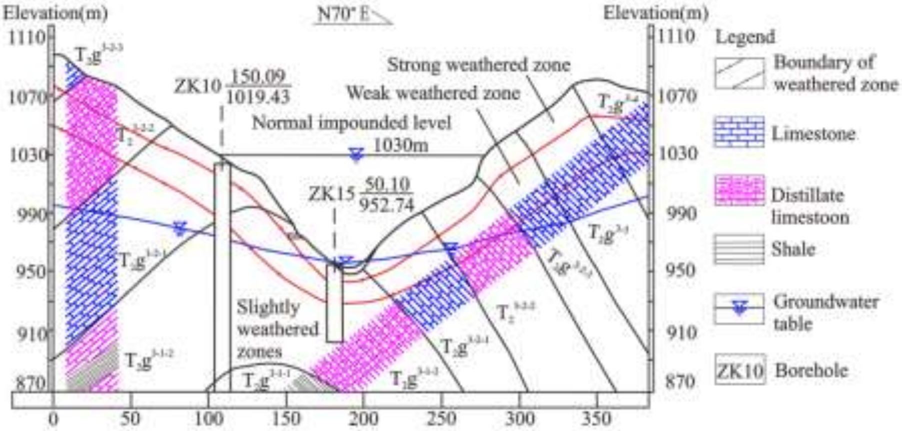
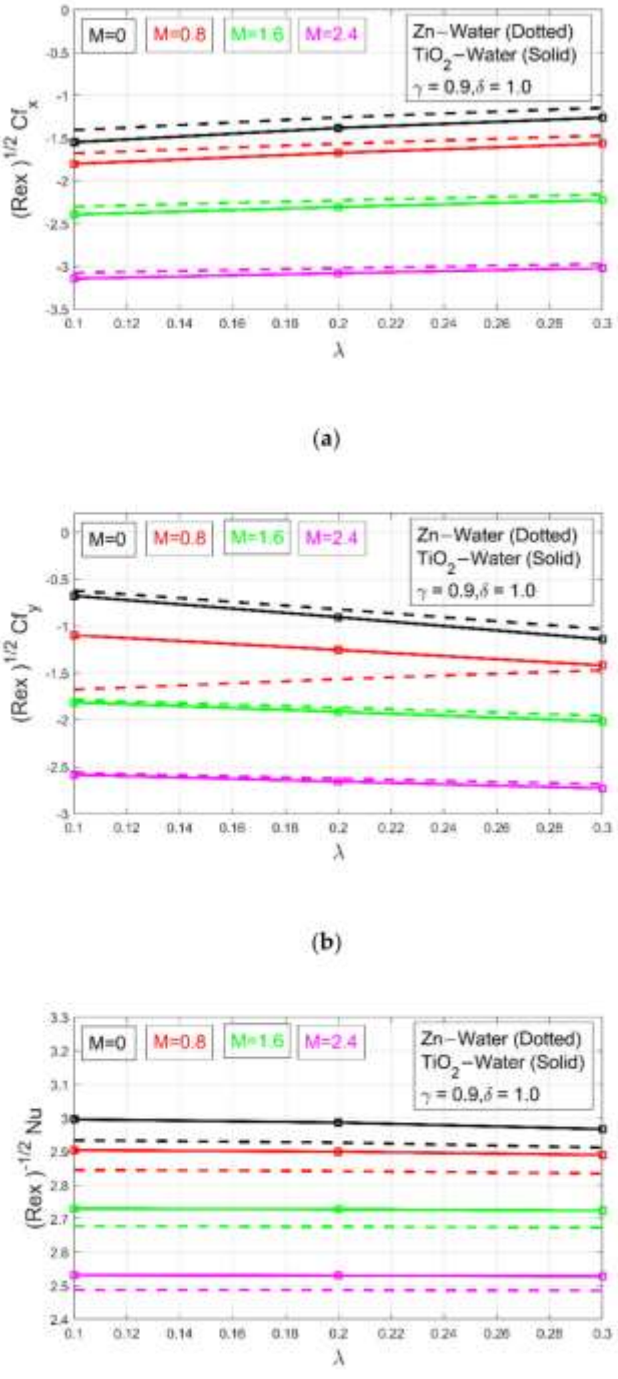


Figure 1 Calculated formation energies and geometric stability of various Cu/ZrO2 interface models.

3.3 Ensemble-Averaged Activity

The microkinetic model compared the single-site method with the statistical ensemble method. The single-site model only uses the Class A structure. It predicts a turnover frequency (TOF) of 1.2×10^{-3} s^{-1}. This value is much lower than the experimental rate. The ensemble model weights the rate of each site by its probability. This method gives a TOF of 1.8×10^{-2} s^{-1}.

Fig. 2 compares these calculated rates with experimental data. As shown in the figure, the ensemble curve matches the experimental measurements well [18]. This match proves that the total activity comes from a mix of different sites, not just one.



(a)

(b)

(c)

Figure 2 Comparison of calculated reaction rates with experimental kinetic data for methanol synthesis under varying conditions.

3.4 Dominant Contribution of Metastable Sites

The "Degree of Rate Control" analysis found the sites that control methanol production. The result shows that stability is different from activity. Class B sites take up less than 30% of the surface area. However, they provide over 65% of the total methanol rate. These sites have a specific Zr–O–Cu bridge structure. This structure lowers the barrier for formate hydrogenation. The stable Class A sites bind intermediates too strongly. This leads to poisoning. The metastable sites bind them with the best strength. This finding confirms that rare surface fluctuations control the catalytic speed.

4.Conclusions

In this paper, a statistical model was built to study the active sites on ZrO_2/Cu catalysts. The method combined DFT energies with Boltzmann statistics. The results show that the surface contains five different types of sites. The analysis indicates that metastable sites are important for the reaction. Even though these sites cover less than 30% of the surface, they provide over 65% of the methanol production rate. This high activity results from their specific structure, which lowers the energy barrier. The ensemble model matches experimental data better than single-site models. This finding confirms that the distribution of sites affects the total rate. This work provides a method to predict the performance of complex catalysts. However, the current model uses a static surface. Future research should consider the dynamic changes of the oxide clusters.

References

[1] Saleh, H. M., & Hassan, A. I. (2023). Green conversion of carbon dioxide and sustainable fuel synthesis. Fire, 6(3), 128.

[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] Kim, J. K., Kim, S., Kim, S., Kim, H. J., Kim, K., Jung, W., & Han, J. W. (2023). Dynamic surface evolution of metal oxides for autonomous adaptation to catalytic reaction environments. Advanced Materials, 35(4), 2203370.

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

[5] Koley, P., Shit, S. C., Yoshida, T., Jampaiah, D., Ariga-Miwa, H., Uruga, T., ... & Bhargava, S. K. (2025). Metal organic framework derived In2O3/ZrO2 heterojunctions with interfacial oxygen vacancies for highly selective CO2-to-methanol hydrogenation. Nature communications, 16(1), 8903.

[6] 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.

[7] Butera, V. (2024). Density functional theory methods applied to homogeneous and heterogeneous catalysis: a short review and a practical user guide. Physical Chemistry Chemical Physics, 26(10), 7950-7970.

[8] Pastor, E., Sachs, M., Selim, S., Durrant, J. R., Bakulin, A. A., & Walsh, A. (2022). Electronic defects in metal oxide photocatalysts. Nature Reviews Materials, 7(7), 503-521.

[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] Deinum, E. E., & Jacobs, B. (2024). Rho of Plants patterning: linking mathematical models and molecular diversity. Journal of Experimental Botany, 75(5), 1274-1288.

[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] Simons, J. F., de Heer, T. J., van de Poll, R. C., Muravev, V., Kosinov, N., & Hensen, E. J. (2023). Structure sensitivity of CO2 hydrogenation on Ni revisited. Journal of the American Chemical Society, 145(37), 20289-20301.

[13] Franco-Pérez, M., Heidar-Zadeh, F., Ayers, P. W., De Proft, F., Vela, A., Gázquez, J. L., & Geerlings, P. (2024). Temperature and external fields in conceptual density functional theory. Chemical Science, 15(48), 20090-20121.

[14] 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.

[15] Peng, M., Li, C., Wang, Z., Wang, M., Zhang, Q., Xu, B., ... & Ma, D. (2025). Interfacial catalysis at atomic level. Chemical Reviews, 125(4), 2371-2439.

[16] Erfani, A., Jafarinejad, T., Roels, S., & Saelens, D. (2024). Impact of dataset sampling period on building thermal models used for flexibility activation. Building and Environment, 262, 111775.

[17] 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.

[18] Militzer, B., Hubbard, W. B., Wahl, S., Lunine, J. I., Galanti, E., Kaspi, Y., ... & Bolton, S. J. (2022). Juno spacecraft measurements of Jupiter’s gravity imply a dilute core. The planetary science journal, 3(8), 185.