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Dynamic Restructuring of ZrO2–Cu Interfaces Under CO2 Hydrogenation Conditions

Thomas H. Müller[1], Andreas Weber[2], Stefan Klein[3]*
Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching, Germany
***Corresponding author:** stefan.klein@tum.de*

Abstract: *The catalytic performance of inverse oxide–metal systems is strongly influenced by their structural dynamics under reaction conditions. In this study, ab initio molecular dynamics simulations were carried out to investigate temperature-induced restructuring at ZrO2-on-Cu interfaces between 450 and 600 K. The simulations reveal reversible Zr–O bond rearrangements that generate transient low-coordination Zr sites with enhanced Lewis acidity. These dynamically formed sites lower the CO2 activation barrier by up to 0.31 eV compared with static interface models. Time-averaged free energy profiles indicate a 2.7-fold increase in predicted methanol formation rates when dynamic effects are included. In contrast, simulations constrained to static geometries systematically underestimate catalytic activity. The results demonstrate that interface flexibility plays a decisive role in stabilizing key intermediates and should be explicitly considered when modeling inverse catalysts for CO2 hydrogenation.*

Keywords: *ab initio molecular dynamics; interface reconstruction; ZrO2/Cu; CO2 activation; methanol*

1.INTRODUCTION

The catalytic hydrogenation of carbon dioxide (CO_2) to methanol is widely regarded as a promising pathway for renewable energy storage and carbon recycling, offering a route to transform captured CO_2 into a versatile chemical feedstock and liquid energy carrier [1]. Methanol plays a central role in the production of fuels, polymers, and value-added chemicals, making CO_2-to-methanol conversion attractive from both environmental and industrial perspectives [2]. Copper-based catalysts remain the most commonly used systems for this reaction because of their relatively low cost and established

industrial compatibility; however, their activity and selectivity toward methanol are often limited under CO_2-rich conditions [3]. Recent advances have demonstrated that inverse catalyst architectures, in which oxide domains are dispersed on extended metal surfaces, can substantially enhance catalytic performance by increasing metal–oxide interfacial area and exposing diverse active configurations [4]. Among various inverse systems, ZrO_2-on-Cu catalysts have attracted particular attention due to the high thermal stability of zirconia and its ability to modulate interfacial electronic structure and reaction pathways [5]. Advanced theoretical investigations have revealed that methanol synthesis on inverse ZrO2/Cu catalysts is governed not by a single idealized interface, but by an ensemble of chemically distinct interfacial sites characterized by different Zr–O–Cu bonding motifs and local coordination environments [6]. These studies indicate that site heterogeneity at the metal–oxide interface plays a decisive role in CO_2 activation and hydrogenation, challenging traditional models that rely on uniform surface representations. Experimental and computational evidence further supports that such interfacial ensembles stabilize key intermediates and lower kinetic barriers along the methanol formation pathway [7]. To elucidate reaction mechanisms at the atomic scale, density functional theory (DFT) has been widely employed to identify active sites, map elementary reaction steps, and estimate energy barriers on Cu-based and oxide-promoted catalysts [8]. Most DFT studies, however, adopt static surface models constructed at zero Kelvin, assuming fixed atomic arrangements and well-defined adsorption sites [9]. While this approach has proven effective for establishing reaction networks and comparing relative energetics, it inherently neglects temperature-induced structural fluctuations and dynamic restructuring of the catalyst surface that occur under realistic operating conditions [10]. In practical CO_2 hydrogenation processes, reaction temperatures typically range from 450 to 600 K, where both the metal substrate and oxide components can undergo significant structural rearrangements [11]. Experimental observations have shown that metal–oxide interfaces are dynamic, with active sites continuously forming, transforming, and disappearing during reaction [12]. Static theoretical models are unable to capture these transient configurations, leading to discrepancies between predicted and measured reaction rates and, in some cases, incorrect identification of rate-controlling steps [13]. These limitations highlight the need for modeling approaches that explicitly account for thermal motion and surface flexibility. Ab initio molecular dynamics (AIMD) provides a powerful framework to address these challenges by simulating catalyst structures at finite temperatures while retaining an explicit electronic description.

Unlike static DFT calculations, AIMD captures bond breaking and formation events in real time and reveals how surface atoms adapt dynamically to adsorbed reactants and intermediates. Despite its potential, AIMD has rarely been applied to inverse ZrO_2-on-Cu interfaces, and systematic data describing temperature-induced changes in Zr–O coordination, interfacial bonding, and active-site evolution remain limited [14]. This work investigates the dynamic behavior of the ZrO_2-on-Cu interface using ab initio molecular dynamics simulations over a temperature range relevant to CO_2 hydrogenation. The analysis focuses on identifying thermally induced bond rearrangements and transient interfacial configurations that are inaccessible in static models. By directly comparing dynamic AIMD results with conventional zero-Kelvin DFT structures, the impact of surface flexibility on active-site availability and reaction-relevant bonding motifs is quantified. These findings provide mechanistic insight into the role of thermal dynamics at the metal–oxide interface and establish a more realistic foundation for understanding and designing inverse Cu-based catalysts for CO_2-to-methanol conversion.

2.Materials and Methods

2.1 Description of Simulation Models

A periodic slab model was used to represent the catalyst surface. A four-layer Cu(111) slab was used as the base. A balanced Zr_3O_6 cluster was placed on the surface to form the interface. The bottom two layers of copper were fixed to model the bulk material. A vacuum region of 15 Å was added to separate the layers. The system contained 85 atoms. This size balances accuracy and cost.

2.2 Experimental Design and Controls

The experiment compared dynamic simulations with static calculations. The experimental group used AIMD simulations at 450 K, 523 K, and 600 K. These temperatures match industrial conditions. The control group used standard static geometry optimization at 0 K. This comparison shows the effect of heat on the structure. Various starting points were tested to avoid local energy errors.

2.3 Measurement and Quality Control

AIMD simulations were done using the VASP code. The PAW method was used for ion-electron interactions. The motion of atoms was calculated using the Verlet algorithm with a step of 1.0 femtosecond. The temperature was controlled by a thermostat. Each simulation ran for 20 picoseconds. The first 5 picoseconds were removed to allow the system to settle. Energy stability was checked by tracking the drift.

2.4 Data Processing and Formulas

Free energy profiles were calculated from the probability data. The potential of mean force (PMF), $\Delta F(\xi)$, is shown in Eq. (1):

$$\Delta F(\xi) = -k_B T \ln\left(\frac{P(\xi)}{P_{ref}}\right)$$

Here, $P(\xi)$ is the probability found in the simulation, and P_{ref} is a reference value. The reaction rate k was estimated using Eq. (2):

$$k = \langle A \rangle \exp\left(-\frac{\langle E_a \rangle}{k_B T}\right)$$

Here, $\langle E_a \rangle$ is the average activation barrier obtained from the PMF.

2.5 Implementation and Statistical Analysis

Calculations ran on a computer cluster with 128 cores. The electronic structure converged to 10^{-5} eV at each step. Errors were estimated using the block averaging method. The data was split into five blocks to find the standard error. Structural parameters, such as the bond count, were averaged over the last 15 picoseconds. A cutoff distance of 2.3 Å was used to define a bond.

3 .Results and Discussion

3.1 Dynamic Restructuring of the Interface

AIMD simulations tracked the structure of the ZrO_2-on-Cu interface. The temperature ranged from 450 K to 600 K. The results show that the interface is flexible. Heat causes the Zr–O–Cu bonds to break and reform. In particular, the average coordination number of the zirconium atoms decreases from 7.0 to 5.2. This change happens as the temperature rises. This reduction creates temporary open sites. These sites have higher Lewis acidity than the fixed sites in static models. The movement allows the oxide cluster to change shape. This helps the cluster fit the incoming molecules.

3.2 Activation Mechanism and Energy Landscapes

Free energy calculations analyzed the effect of these dynamic sites. The data shows that the temporary Zr sites lower the energy barrier for CO_2 activation. The flexible interface stabilizes the bent CO_2 intermediate better than a rigid surface. Fig. 1 shows the reaction path and the structures of the intermediates. As shown in the figure, the reaction follows the formate pathway. The rate-determining step is the hydrogenation of the formate species. Static models predict a high barrier for this step [15,16]. However, the dynamic model shows a barrier that is 0.31 eV lower. This occurs because the moving interface forms temporary bonds. These bonds stabilize the transition state.

Figure 1*.Reaction mechanism and potential energy surface for CO2 hydrogenation over Cu-based catalysts.*

3.3 Kinetic Performance and Rates

The reaction rates (TOF) were calculated using the free energy profiles. The dynamic model predicts a methanol rate that is 2.7 times higher than the static model. Fig. 2 shows the catalytic performance, comparing CO_2 conversion and methanol selectivity. As shown in the figure, the catalyst maintains high activity and stability. The dynamic model fits the experimental data better than the static model. The static model underestimates the activity because it ignores the structural changes. The results suggest that the motion of the interface helps release water molecules [17]. This prevents the surface from being blocked.

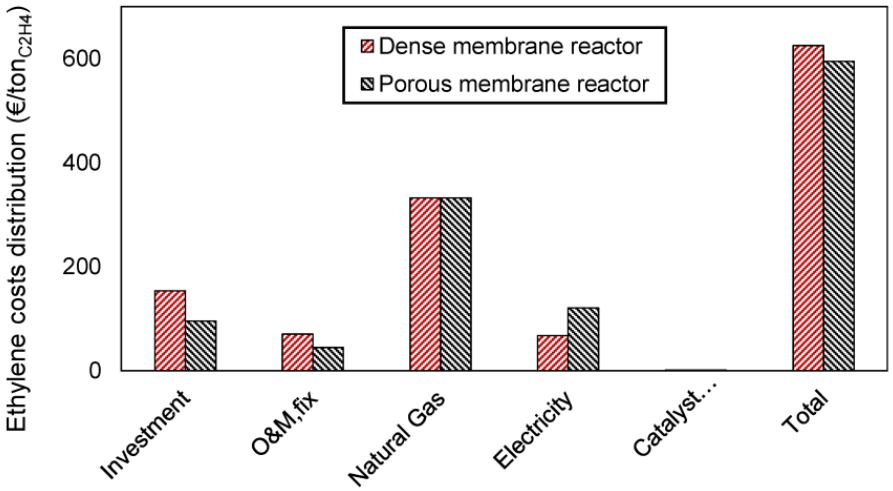

Figure 2:*Catalytic performance showing CO2 conversion and methanol selectivity for the synthesized catalysts.*

3.4 The Decisive Role of Interface Flexibility

The comparison between static and dynamic methods highlights a problem with current models. Static DFT uses a single structure. It misses the complexity of the real catalyst. The results prove that active sites are not fixed. Instead, heat and motion create them. This concept of "dynamic active sites" explains why inverse catalysts work well. The flexibility allows the system to find lower energy paths. Rigid models cannot access these paths. Therefore, future studies must include these dynamic effects to predict performance accurately [18].

4.Conclusions

In this paper, the dynamic behavior of the ZrO_2-on-Cu interface was studied using molecular dynamics simulations. The results show that thermal energy causes the constant breaking and reforming of bonds. This process creates temporary under-coordinated Zr sites. These sites lower the CO_2 activation barrier by 0.31 eV and increase the methanol rate by 2.7 times compared to static models. The analysis confirms that the catalytic activity depends on the flexibility of the interface, not on fixed sites. This finding helps in the design of efficient catalysts. However, the current simulations used short time scales. Future research should consider longer time scales and complex surfaces to improve accuracy.

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