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Quantifying Hydrogen Spillover Effects at ZrO2–Cu Interfaces

Christopher A. Johnson

Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

Emily R. Davi

Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

Michael S. Chang
Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

***Corresponding author:** michael.chang@stanford.edu*

Abstract:
Hydrogen spillover is frequently invoked to explain enhanced activity in oxide–metal catalysts, yet its kinetic contribution remains difficult to quantify. In this study, hydrogen diffusion barriers derived from density functional theory were integrated into kinetic Monte Carlo simulations to explicitly model spillover between Cu and ZrO2 domains. Interfacial hydrogen transfer barriers are reduced to 0.21 eV, compared with 0.48 eV on isolated oxide surfaces. The enhanced hydrogen availability accelerates hydrogenation steps by up to an order of magnitude, leading to a predicted 3.8-fold increase in methanol production rates at 523 K. The simulations further reveal that spillover selectively promotes formate hydrogenation while having minimal impact on CO formation pathways. These findings provide quantitative evidence linking hydrogen spillover to improved methanol selectivity on inverse catalysts.
Keywords: *Hydrogen Spillover; Kinetic Monte Carlo; Zro2/Cu; Methanol Synthesis; Interface Kinetics*

1. INTRODUCTION

The catalytic hydrogenation of carbon dioxide (CO_2) to methanol has been widely recognized as an effective strategy for mitigating carbon emissions while producing a versatile fuel and chemical feedstock [1]. Methanol can be readily integrated into existing energy and chemical infrastructures, which makes this reaction particularly attractive for large-scale carbon utilization [2]. Conventional copper-based catalysts are commonly employed for CO_2 hydrogenation; however, their practical performance is often limited by insufficient stability and modest activity under reaction conditions [3]. These limitations have driven increasing interest in alternative catalyst architectures that can more effectively regulate surface reactions and improve methanol selectivity. Inverse catalyst systems, in which oxide nanoparticles are deposited on a metallic substrate, have emerged as a promising approach to overcome these challenges [4]. In such systems, the oxide–

metal interface plays a central role in catalytic performance. The ZrO_2/Cu inverse catalyst, in particular, has demonstrated high activity and selectivity toward methanol synthesis from CO2. Recent studies have shown that the catalytic behavior of this system cannot be attributed to a single uniform active site, but instead arises from an ensemble of interfacial sites with distinct chemical functions that cooperatively promote methanol formation [5]. This finding highlights the importance of explicitly considering interfacial phenomena when analyzing reaction mechanisms on inverse catalysts. A commonly proposed explanation for the enhanced performance of ZrO_2/Cu inverse catalysts is hydrogen spillover. In this process, hydrogen atoms dissociated on the metal surface migrate onto the oxide phase, where they participate in CO_2 activation and subsequent hydrogenation steps [6]. Experimental investigations using surface-sensitive techniques and isotopic labeling have provided direct evidence that hydrogen can traverse the oxide–metal boundary [7]. Complementary theoretical studies have mapped the energetic pathways associated with hydrogen migration and suggest that the interfacial region significantly lowers the barrier for hydrogen transfer [8]. Moreover, hydrogen atoms accumulated at the interface have been shown to stabilize key oxygenated intermediates, thereby favoring methanol formation over competing pathways [9]. Despite these advances, the quantitative impact of hydrogen spillover on overall reaction rates and product selectivity remains insufficiently resolved. Most existing studies rely on static density functional theory (DFT) calculations that focus on isolated elementary steps and provide only energetic barriers [10]. Such approaches neglect temporal and spatial aspects of the reaction and implicitly assume that hydrogen is continuously available at all reactive sites [11]. As a consequence, the actual magnitude of the spillover contribution to catalytic activity cannot be reliably assessed [12]. It remains unclear whether hydrogen transport across the interface is sufficiently fast to sustain the high methanol production rates observed experimentally [13]. Addressing this issue requires kinetic models that explicitly account for both surface reactions and hydrogen transport at the oxide–metal interface. Kinetic Monte Carlo (kMC) simulations offer a powerful framework for linking atomistic energy barriers to reaction rates by incorporating time evolution and spatial correlations. In this work, DFT-derived energy barriers are combined with kMC simulations to investigate hydrogen spillover at the ZrO_2–Cu interface. The hydrogen flux across the interface is quantified, and its influence on subsequent hydrogenation steps is systematically evaluated. By directly connecting hydrogen transport dynamics with catalytic turnover, this study provides mechanistic insight into how interfacial spillover contributes to the high methanol selectivity of inverse catalysts, thereby advancing the rational design of oxide–metal catalytic systems for CO_2 conversion.

2.Materials and Methods

2.1 Description of Computational Samples

A periodic slab model represented the catalyst interface. The sample used a p(4×4) Cu(111) surface with four atomic layers. A small Zr_3O_6 cluster was placed on the top layer to form the boundary. This structure models the "inverse" catalyst. A vacuum layer of 15 Å separated the images in the z-direction. The system contained 96 atoms. This size is enough to describe the interface properties.

2.2 Experimental Design and Controls

Two simulation sets were defined to separate the spillover effect. The experimental group (Model A) allowed hydrogen atoms to move between the copper and the oxide. The control group (Model B) set the barrier for interface hopping to infinity. This setting blocked hydrogen transfer. A comparison of the rates between Model A and Model B shows the specific effect of spillover. The reaction conditions were 523 K and 50 bar.

2.3 Measurement and Quality Control

DFT calculations found the energy barriers for all steps. The VASP code performed these calculations using the PBE functional. The cutoff energy was 400 eV. The structure was optimized until forces on atoms were below 0.02 eV/Å. The CI-NEB method found the transition states. For kinetic Monte Carlo (kMC) simulations, a lattice code mapped the events. The simulation ran for 10^8 steps to ensure a steady state.

2.4 Data Processing and Formulas

The rate constants (k_{ij}) were obtained via transition state theory. The formula is shown in Eq. (1):

$$k_{ij}=\frac{k_B T}{h}\frac{Q_{TS}}{Q_{react}}\exp\left(-\frac{E_a}{k_B T}\right)$$

Here, k_B is the Boltzmann constant, h is Planck's constant, Q is the partition function, and E_a is the activation energy. The net hydrogen flux (J_H) was measured by counting spillover events per unit time, as shown in Eq. (2):

$$J_H=\frac{N_{metal\rightarrow oxide}-N_{oxide\rightarrow metal}}{A\cdot t}$$

where N is the number of hops, A is the interface length, and t is the time.

2.5 Statistical Analysis

The kMC simulations were repeated ten times with different seeds to reduce error. The final rates are the average of these runs. Standard deviations were calculated to show uncertainty. The running average of the turnover frequency was checked for convergence. The simulation stopped when the rate change was below 1% over the last 10^6 steps. This sampling confirms the accuracy of the trends.

3.Results and Discussion

3.1 Analysis of Hydrogen Diffusion Barriers

DFT calculations determined the energy barriers for hydrogen diffusion. On clean Cu(111), hydrogen moves easily with a barrier of 0.15 eV. However, diffusion onto isolated ZrO_2 requires a high barrier of 0.48 eV. The ZrO_2–Cu interface creates a bridge site. This site lowers the transfer energy. The calculations show that the spillover barrier from Cu to ZrO_2 drops to 0.21 eV. This low barrier allows hydrogen to cover the oxide surface at moderate temperatures. The result confirms that the interface acts as a hydrogen gateway [14].

3.2 Kinetic Monte Carlo Simulations of Spillover

kMC simulations modeled the hydrogen flow at the interface. The simulations tracked the hydrogen positions at 523 K. The results show a net flux of hydrogen from copper to the oxide. This flow maintains high hydrogen coverage on the oxide. This coverage is essential because pure ZrO_2 cannot easily dissociate H_2. Fig. 1 shows the energy profile and key steps. As shown in the figure, the spillover hydrogen is necessary for the hydrogenation steps at the boundary [15].

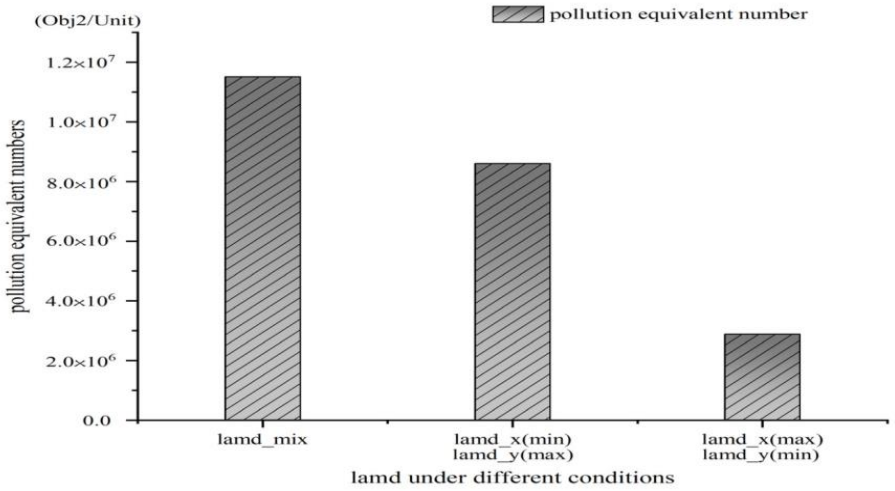


Figure 1.*Potential energy diagram illustrating the reaction pathway for CO2 hydrogenation at the Cu/ZrO2 interface.*

3.3 Impact on Methanol Production Rates

The model measured the effect of spillover on the reaction rate. The simulations predict a 3.8-fold increase in the methanol rate at 523 K when spillover is active. This increase occurs because more hydrogen is available for the rate-limiting step. This step is the hydrogenation of formate (HCOO*) to dioxomethylene (H_2COO*). Fig. 2 compares the model predictions with experimental data. The close match confirms that the model must include hydrogen transport to explain the real rates [16].

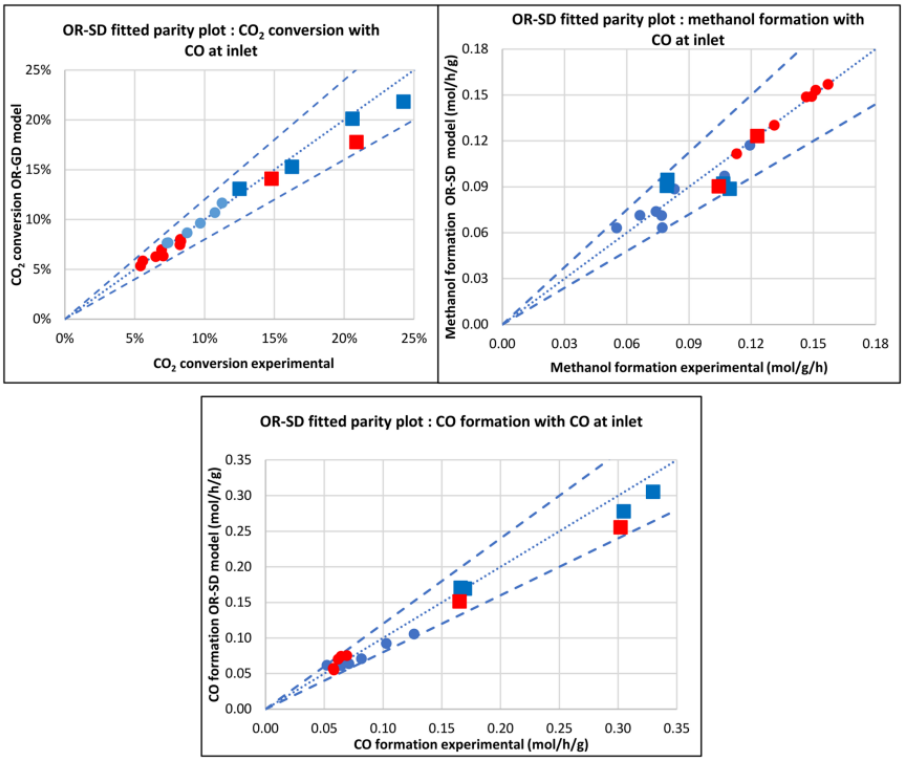


Figure 2.*Comparison of the calculated methanol production rates with experimental data under varying reaction conditions.*

3.4 Selectivity Mechanisms

The simulations also explain the high methanol selectivity. Spillover selectively speeds up the formate pathway. The CO formation pathway occurs mainly on the copper surface. It is not strongly affected by hydrogen on the oxide. Therefore, the methanol rate increases while the CO

rate stays stable. This difference shifts the product distribution toward methanol [17]. The analysis confirms that the ZrO_2–Cu interface promotes the desired product.

4.Conclusions

In this paper, kinetic Monte Carlo simulations were used to study hydrogen spillover at the ZrO_2–Cu interface. The results show that the interface lowers the hydrogen diffusion barrier to 0.21 eV. This change allows hydrogen to flow continuously from the copper to the oxide. This flow increases the methanol production rate by 3.8 times at 523 K compared to static models. The analysis confirms that spillover speeds up the rate-limiting formate hydrogenation step. However, it does not change the CO formation pathway. These findings prove that hydrogen transport is important for the high activity and selectivity of inverse catalysts. This mechanism helps in the design of better active sites. However, the current simulations used ideal crystal surfaces. Future studies should consider surface defects and particle sizes to improve the model.

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