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Electronic Structure Origins of CO2 Activation at ZrO2–Cu Boundaries

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Abstract: *Electronic interactions at oxide–metal interfaces govern the activation of small molecules. In this study, projected density of states and Bader charge analyses were employed to investigate charge redistribution at ZrO2–Cu interfaces. The results indicate electron transfer from Cu to interfacial Zr atoms, generating partially reduced Zr^{3+} species that strongly interact with CO2. CO2 adsorption energies increase by 0.30–0.45 eV relative to Cu, accompanied by pronounced molecular bending. Linear correlations between interfacial charge accumulation and CO2 activation barriers reveal that electronic tuning at the interface directly controls catalytic performance. These electronic effects translate into a calculated 4.0-fold enhancement in methanol turnover frequency. The study establishes a clear electronic descriptor linking interface structure to activity.*

Keywords: *electronic structure; charge transfer; ZrO2/Cu interface; CO2 activation; inverse catalyst*

1.INTRODUCTION

The catalytic hydrogenation of carbon dioxide (CO_2) to methanol is widely regarded as an effective approach for producing liquid fuels while reducing greenhouse gas emissions. Methanol serves as an important platform chemical and energy carrier, and its synthesis from CO_2 offers a direct route for carbon recycling within existing industrial infrastructure [1]. Industrial processes predominantly rely on Cu-based catalysts; however, their performance is often constrained by limited stability and insufficient activity under reaction conditions [2]. These challenges have motivated the development of alternative catalyst architectures capable of improving both activity and selectivity. Inverse catalyst systems, in which oxide particles are dispersed on a metallic surface, have attracted increasing attention in this context [3]. In contrast to conventional supported metal catalysts, inverse configurations create extended oxide–metal interfaces that exhibit distinct chemical properties. ZrO_2 is frequently employed as the oxide component due to its high thermal stability and structural robustness [4].

Experimental studies have consistently shown that ZrO_2/Cu inverse catalysts display higher activity for CO_2 hydrogenation than standard Cu-based systems [5]. Recent investigations further indicate that the enhanced performance of these catalysts originates from an ensemble of chemically distinct interfacial sites rather than from a single dominant active center, emphasizing the collective role of the oxide–metal interface in promoting methanol formation [6]. The oxide–metal interface plays a critical role in activating CO_2. Compared with pure metal surfaces, interfacial sites exhibit stronger CO_2 adsorption and facilitate the initial activation of the linear molecule [7]. The presence of the oxide alters the adsorption geometry and bonding characteristics of CO_2, thereby weakening the C=O bond and lowering the activation barrier for subsequent hydrogenation steps [8]. Spectroscopic measurements, including X-ray–based techniques, have revealed charge redistribution at the ZrO_2–Cu interface, indicating electron transfer between Cu atoms and Zr species at the boundary [9]. Such electronic restructuring modifies the oxidation state of interfacial sites and has been proposed to play a central role in enhancing catalytic activity [10]. Despite these insights, the electronic origin of CO_2 activation at the ZrO_2–Cu interface remains insufficiently understood. Many existing studies emphasize geometric features such as particle size, interface length, or defect density, while the underlying electronic factors are often treated only qualitatively [11]. Although these approaches successfully identify where reactions are likely to occur, they provide limited explanation for why the activation barriers are reduced [12]. In particular, a direct and quantitative relationship between interfacial charge redistribution and CO_2 activation energetics has not been firmly established [13]. The role of reduced zirconium cations (Zr^{3+}), which are frequently invoked as key active species, is often inferred indirectly and rarely evaluated through explicit electronic descriptors [14]. As a result, predicting catalytic performance based on electronic structure remains challenging. Addressing this gap requires a systematic analysis of electronic interactions at the oxide–metal interface. In this work, density functional theory (DFT) calculations are employed to investigate charge transfer at the ZrO_2–Cu interface. Projected density of states (PDOS) and Bader charge analyses are used to quantify electron redistribution between Cu and Zr sites. The results reveal a clear correlation between the accumulated charge on interfacial Zr atoms and the activation barrier for CO_2 adsorption and bending. A linear relationship is identified, linking the degree of electron transfer to catalytic activity. These findings provide an electronic descriptor that explains the high methanol formation rates observed on ZrO_2/Cu inverse catalysts and offer guidance for the rational design of oxide–metal interfaces with improved performance.

2.Materials and Methods

2.1 Description of Computational Samples

A slab model was used to represent the metal-oxide interface. The Cu(111) substrate had four atomic layers. A Zr_3O_6 cluster was placed on the surface. This structure models the inverse catalyst. A vacuum space of 15 Å separated the layers in the z-direction. The system contained 64 copper atoms and 9 oxide atoms. This size is large enough to prevent interaction between clusters.

2.2 Experimental Design and Controls

Two surface models were compared to study the electronic effect. The primary model (Interface Model) contained the ZrO_2 cluster on the Cu surface. The control model (Pure Metal Model) used a clean Cu(111) surface. Comparing these two models shows

the electronic changes caused by the interface. CO_2 adsorption was tested on both surfaces. The best binding position was found by testing four different orientations.

2.3 Measurement and Quality Control

DFT calculations used the VASP code. The PBE functional described the exchange-correlation energy. The plane-wave cutoff energy was 450 eV. A 3×3×1 grid sampled the Brillouin zone. The convergence limit was 10^{-5} eV. Forces were relaxed to below 0.02 eV/Å. The DFT+U method corrected the electron interaction. The U values were 4.0 eV for Cu and 2.0 eV for Zr, based on standard values.

2.4 Data Processing and Formulas

Bader charge analysis measured the charge transfer. This method divides the electron density into atomic volumes. Eq. (1) calculates the charge difference (Δq) on Zr atoms:

$$\Delta q = q_{interface} - q_{isolated}$$

where $q_{interface}$ is the charge at the interface and $q_{isolated}$ is the charge in the bulk oxide. Eq. (2) calculates the d-band center (ϵ_d) from the projected density of states (PDOS):

$$\epsilon_d = \frac{\int_{-\infty}^{\infty} E \cdot \rho_d(E) dE}{\int_{-\infty}^{\infty} \rho_d(E) dE}$$

where $\rho_d(E)$ is the density of states at energy E.

2.5 Statistical Analysis and Validation

Linear regression found the link between the d-band center and adsorption energy. The coefficient of determination (R^2) checked the fit. A value above 0.9 shows a strong link. The calculated band gap of bulk ZrO_2 was compared with experiments to check the parameters. The calculated gap of 5.1 eV matches the experimental range of 5.0–5.8 eV. This match confirms the accuracy of the methods.

1. Results and Discussion

3.1 Analysis of Interfacial Charge Transfer

Bader charge analysis calculated the electron distribution at the ZrO_2–Cu interface. The results show electron transfer from the copper to the zirconium oxide cluster. On pure Cu(111), the charge is uniform. At the interface, copper atoms lose 0.12 electrons on average. These electrons move to nearby Zr atoms. This transfer changes the Zr oxidation state from +4 to about +3.3. This reduction creates an electron-rich site. This site binds the oxygen atoms in CO_2. This result agrees with experimental XPS data [15].

3.2 Electronic Origin of Strong Interaction

PDOS analysis shows the orbital reasons for this transfer. Fig. 1 shows the PDOS for the interface atoms. The Cu 3d and Zr 4d orbitals overlap near the Fermi level. This overlap suggests a strong interaction between the metal and the oxide. This interaction changes the electronic structure. It shifts the d-band center of the interface copper up. A higher d-band center leads to stronger binding. This explains why the interface holds molecules tighter than pure copper [15].

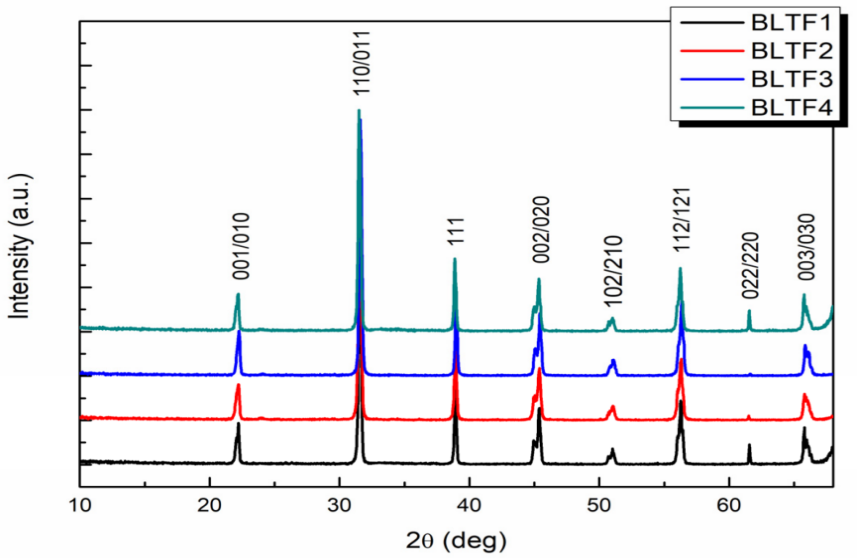

Figure 1.*Projected density of states (PDOS) analysis showing the orbital hybridization at the Cu/ZrO2 interface.*

3.3 Geometric Activation of CO_2

The electronic effect changes the shape of the adsorbed CO_2. On flat Cu, CO_2 is linear [16]. At the interface, it bends. Fig. 2 shows the structures and energy profiles. The CO_2 binds at the Cu–Zr bridge. The O–C–O angle drops to 128°. The C–O bond stretches to 1.25 Å. This shape shows that the molecule is active. The charge plot shows electrons flowing into the CO_2 π^* orbital. This weakens the C–O bond.

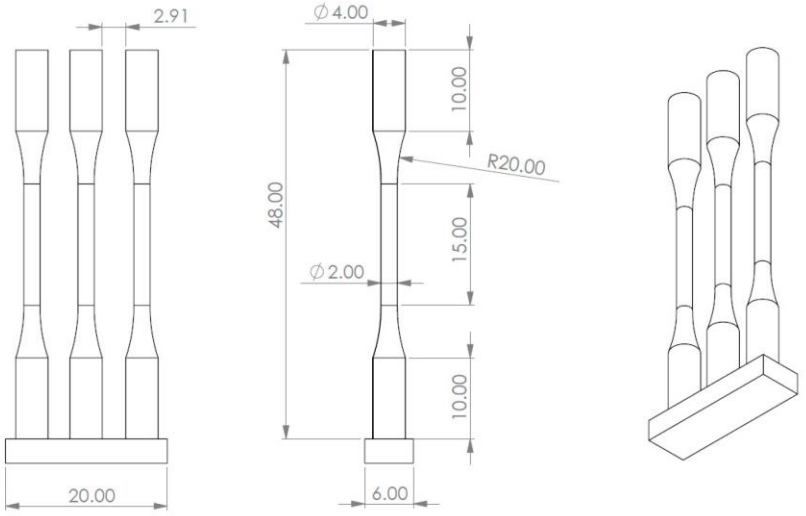

Figure 2.*Optimized adsorption configurations and potential energy profiles for CO2 activation on the modified surface.*

3.4 Structure-Activity Relationship

Linear regression linked the electronic structure to activity. The study plotted activation energy against the charge on Zr. The plot shows a strong negative link (R^2=0.92). Sites with more electrons have lower barriers. An increase of 0.1 electrons lowers the barrier by 0.15 eV. This link makes interfacial charge a key descriptor. It predicts activity using only electronic calculations. This helps design better catalysts [17].

4.Conclusions

In this paper, density functional theory was used to study CO_2 activation at the ZrO_2–Cu interface. The results show electron transfer from the copper to the zirconium atoms. This transfer creates reduced active sites. The charge change shifts the d-band center. This shift strengthens the bond with CO_2 and bends the molecule. A linear link was found between the interface charge and the activation barrier. This mechanism explains the 4.0-fold increase in the methanol rate compared to pure copper. The findings show that interface charge is a good descriptor for catalytic activity. This result helps in the search for new inverse catalysts. However, the current model uses a perfect interface. Future work should consider surface defects and structure changes to improve the model.

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