The Influence of Hubbard U Parameter in Simulating Adsorption and Reactivity on CuO: A Combined Theoretical and Experimental Study

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ABSTRACT: Transition metal oxides are an important class of catalytic materials widely used in the chemical manufacturing and processing industry owing to their low cost, high surface area, low toxicity and easily tunable surface and structural properties. For these strongly correlated transition metal oxides, standard approximations in the density functional theory (DFT) exchange-correlation functional fail to describe the electron localization accurately due to the intrinsic errors arising from electron self-interactions. DFT+U method is a widely used extension of DFT, where the Hubbard U term is an onsite potential which puts a penalty on electron delocalization, successfully describing such systems at only slightly higher computational cost than standard DFT methods. The U-value is usually chosen based on its accuracy in reproducing bulk properties like lattice parameters and band structure. However, chemical reactions on transition metal oxide surfaces involve complex surface-adsorbate interactions and using the bulk properties based U-values in a locally changing surface environment may not describe reaction energetics correctly. Hence, in the current DFT+U benchmarking work, using CuO as a model transition metal oxide, we perform DFT+U calculations to investigate the dissociative chemisorption of H₂ on it. It is observed that the U-value impacts computed adsorption enthalpies by over 100 kJ mol⁻¹. The DFT+U calculated adsorption enthalpy is compared with the experimental adsorption enthalpy, and equilibrium adsorption configurations are confirmed using infrared analysis. We reveal that the commonly used U-value of 7 eV (fitted against CuO bulk properties) overestimates the adsorption enthalpy by 20-40 kJ mol⁻¹. The U-value between 4.5-5.5 eV correctly predicts the adsorption of H₂ on CuO. The DFT+U benchmarking procedure elucidated in this article, encapsulates surface-adsorbate interactions, surface reactivity, and the dynamic surface reaction environment and thus, provides an appropriate U-value to be used to model reactions on metal oxide surfaces.
1. Introduction

1.1 Transition metal oxides and CuO

Transition metal oxides (TMOs) are extensively used as catalysts in many industrial processes such as chemical looping combustion\textsuperscript{1-4}, selective oxidation and dehydrogenation reactions like catalytic oxidation of methanol to formaldehyde\textsuperscript{5} or propene to acrolein\textsuperscript{6} and applications like gas sensors\textsuperscript{7} and nanoelectronics\textsuperscript{8}. TMOs are also incorporated into zeolites as active sites to alter and control their activity and selectivity for different applications\textsuperscript{9-11}. In TMOs, the overlapping 2p-orbitals of oxygen form the low energy valence band, which is highly populated; whereas the overlapping d orbitals of the transition metal form the conductance band, which is mainly responsible for their diverse electronic and magnetic properties.

Cupric Oxide (CuO), is one such extensively used and studied TMO, in both pure and supported forms, not only in industrial processes like Chemical-looping Combustion\textsuperscript{4} but also for various applications such as lithium ion batteries\textsuperscript{12-13}, supercapacitors\textsuperscript{14-16} and gas sensors\textsuperscript{17-18}. Recently, CuO in both pure and supported forms, has been shown (i) to activate the formyl C-H bond to convert glucose to gluconic acid\textsuperscript{19-20} for biomass oxidation reactions, (ii) to be a suitable material for C-H bond activation\textsuperscript{21}, via multiple mechanisms over its different facets, and (iii) to be highly selective for desired products (imine derivatives) under solvent-free conditions by oxidative coupling of aromatic amines\textsuperscript{22}. The role of active species (Cu-O-Cu) in Cu-exchanged mordenite has also been examined for the selective oxidation of methane to methanol\textsuperscript{23}. These studies provide mechanistic insights into the C-H bond activation, which is central in paving the way for novel processes and catalysts to be used in value-added C\textsubscript{1} chemical processing.
Most of the TMO catalyzed hydrocarbon oxidation reactions are believed to occur primarily via the Mars-Van Krevelen type mechanism\textsuperscript{24-25} with nucleophilic oxidation\textsuperscript{26} (consumption of lattice oxygen\textsuperscript{27}). Catalytic properties of TMOs are largely dependent on its surface characteristics such as, but not limited to, the degree of unsaturation of the surface, the surface acid-base characteristics, the adsorbate-surface interactions, the binding energy of lattice oxygen and the ease of vacancy formation and the presence of cationic and anionic vacancies\textsuperscript{28}. Hence, it is important to study and understand the influence of surface characteristics on the catalytic activity of TMOs, to guide the design and development of efficient and novel TMO based catalysts.

1.2 Density functional theory (DFT) to investigate TMOs and its limitations

Under reaction conditions, TMO surface experiences a dynamic environment due to various parallel and sequential reaction steps like adsorption/desorption, oxidation/reduction, and the diffusion of intermediates from one site to the other. This makes it challenging for experimental surface characterization techniques to comment on mechanistic details of the reaction. Hence, computational techniques like Density Functional Theory (DFT) are extensively used as a complementary and predictive tool to investigate the structural, magnetic, and electronic properties of such systems. DFT is used to examine the electronic structure of TMO surfaces, adsorption configurations, reaction pathways and energetics and to identify and predict the elementary reaction steps which govern reaction rates and product selectivity.

In strongly correlated systems like TMOs, due to the localized nature of electrons, the interelectronic interaction is strong, and dynamics of each electron is influenced by and correlated to all other electrons in the system. For such systems, the exchange-correlation (XC) functional approximations in DFT fall short to accurately capture the exchange and correlation effects, leading to difficulties in accounting for electron localization. The description of the
electron-electron interaction leads to a systematic difficulty for DFT calculations, arising from the unphysical interaction of an electron with itself, resulting into an over-delocalization of the electron density. For systems with highly delocalized electrons, the XC functional approximations like the Local density approximation (LDA) and the Generalized gradient approximation (GGA) perfectly cancel out the self-interaction errors (SIEs) arising due to the electron-electron repulsion term, hence correctly describing the electronic structure of systems like metals. However, in systems with strongly correlated electrons and localized states, unequal cancellations of these errors lead to over-delocalization of electrons and underestimation of the band gaps. Hence, a material being insulator or semiconductor could be incorrectly predicted to have a metallic ground state by DFT calculations. This inaccurate description of the electronic structure of strongly correlated materials with partially or entirely localized outer shell electrons is a long-standing challenge for DFT.

1.3 Extension to DFT methods to describe correlated systems: DFT+U

Over the years, numerous methods have been developed to treat SIEs and electron delocalization for strongly correlated systems such as self-interaction correction (SIC) methods, DFT+U method, Hybrid functionals as well as more accurate, computationally expensive methods like Reduced Density Matrix Theory and Dynamical Mean Field Theory. Among these, two popular and widely used methods for catalytic surface applications are, (i) DFT+U, in which an onsite Coulomb correction potential, U, is introduced as an energy penalty on the delocalization of electrons, thus restricting the amount of delocalization done by standard DFT methods, and (ii) Hybrid functionals, which involve mixing of non-local (exact Fock exchange) and semi-local DFT exchange energy, in different percentages. Jacobs ladder ranks the density functional approximations in order of increasing accuracy and sophistication, with Hartree approximation ($E_{xc}=0$) being the least accurate. Semi-local approximations like
LDA and GGA, being more precise, occupy the initial levels of this ladder, whereas, non-local approximations like hybrid functionals belong to the higher levels because of their increased sophistication (and accuracy). DFT+U is the most widely used method to correct the self-interaction errors due to its (i) add-on nature, leading to easy implementation, (ii) easy inclusion and calculation for first and second derivatives of energy such as atomic forces, stresses and atomic force constants\(^3\) (iii) marginal additional costs involved over standard DFT methods, making it computationally less demanding than other higher level functionals.

The DFT+U method to treat SIEs in strongly correlated systems was first established by Anisimov et al.\(^3\). Dudarev et al.\(^3\) bridged this orbital-dependent expression with the rotationally invariant functional proposed by Liechtenstein\(^3\) and came up with the most extensively used form of DFT+U total energy calculations, which in its orbital form is

\[
E_{\text{GGA+U}} = E_{\text{GGA}} + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma} \left[ \left( \sum_m n^\sigma_{m,m} \right) - \left( \sum_{m,m'} n^\sigma_{m,m'} n^\sigma_{m',m} \right) \right]
\]

(1)

where \( \bar{U} \) and \( \bar{J} \) are the screened averaged on-site coulomb repulsion and exchange interaction parameters, respectively. The occupation number of a d-orbital is represented by \( n_m \), with subscripts \( m, m' \) representing the angular momentum quantum number (-2 to +2) for different d orbitals with spin signified by \( \sigma = (1 or -1) \). In this approach, \( U_{\text{eff}} \) replaces \( \bar{U} - \bar{J} \) as the overall net potential term. In other words, \( U_{\text{eff}} \) is the net penalty function which improves the occupancy of certain orbitals by forcing electron localization in the description of strongly correlated systems by DFT+U. From here onwards, we refer to \( U_{\text{eff}} \) as \( U \).

Rohrbach et al.\(^3\) compared the DFT+U method for LDA and GGA functionals for a few transition metal sulfides (MnS, FeS) and stated that a larger U-value is required to compensate for the overbinding characteristic of the LSDA(Local spin-density approximation, an extension of LDA to include electronic spin), which leads to widening of the energy gap, in disagreement
with the photoemission spectra. They concluded that DFT+U with GGA, to be a better descriptor for the functional.

### 1.4 Determining the U-value for TMOs

Although the physical interpretation of the U-value as an onsite potential to restrict the electron delocalization among the neighboring sites might be straightforward, the parameter value can be either determined *ab initio* from DFT calculations, or more commonly selected in a semi-empirical way by its ability to computationally reproduce experimentally measured system properties such as band gap, band structure, metal-metal or metal-oxygen bond distances, lattice parameters and magnetic moments. In the first approach, U value is computed using the second derivative of the DFT computed energy with respect to orbital occupations, rendering the DFT+U calculation completely *ab initio*. Amongst the most common *ab initio* methods used to determine the U value are constrained random phase approximation (cRPA), and linear-response constrained DFT. Some discrepancies have been observed in the U value provided by both these methods, particularly towards the end of 3d metal series, even though theoretically they ought to give the same results. Although significant work is being done in this approach to get a robust procedure to determine the U-value for transition metal compounds, the second approach based on the fitting of experimental data remains widely practiced and accepted. Although popular, the general observation in this approach is that no single U-value perfectly reproduces all the experimental bulk properties of a material. A U-value which either predicts one selected property of interest accurately or minimizes the overall error in predicting a combination of different properties is chosen, leading to different U values for the same TMO like CuO. Capdevila-Cortada et. al. have done significant work in evaluating the performance of DFT+U approaches in studying catalytic systems and also summarized U values available in the literature for different
TMOs. Another interesting aspect of this implementation is that all the properties mentioned above are bulk properties of the system. Hence using the bulk-determined U-value in a locally changing surface environment, which involves structural transitions along a reaction coordinate or changing physical conditions, may cause significant errors in the calculated energetics.\textsuperscript{43, 52-55}

The U-value for strongly correlated systems is also determined by fitting bulk redox energies instead of bulk structural or electronic properties. Wang et al.\textsuperscript{52} determined the bulk experimental oxidation enthalpies (from the thermodynamic tables) for TMOs (FeO, NiO, MnO, etc.) and compared those with the theoretically computed enthalpies for incremental U values using DFT+U. Lutfalla et al.\textsuperscript{53} measured the bulk reduction enthalpies of oxides of Ti, V, Mn, and Ce with H\textsubscript{2} and compared those with the reaction enthalpies computed systematically using DFT+U. Aykol et. al.\textsuperscript{56} derived the local environment dependent (LD) U value based on the transition metal’s oxidation states and coordinating ligand contributions, by comparing the DFT+U calculated energies with the experimental bulk reaction/formation energies (from thermodynamic tables) of 3d metals (Ti, V, Cr, Mn, Fe, Co and Ni) in their oxides and fluorides form. The U-value which replicated the bulk redox energies with sufficient accuracy was chosen to be the U-value for the TMO system. Curnan et. al.\textsuperscript{57} calculated the U value based on its ability to accurately predict the experimental relative energy of ordering of various TiO\textsubscript{2} polymorphs.

Bennett et. al.\textsuperscript{58} showed that U-value affected adsorption energies of different species differently on CeO\textsubscript{2} and presented a theoretical model to predict the U-value based on the average change in the adsorption energy and its gradient for various probe molecules with respect to U. Based on the stationary points in the above model, adsorbates were split into four classes, with one extreme being the adsorptions which involved no orbital overlap or charge transfer, leading to no influence of U-value on the adsorption energies, while the other extreme
involved reduction of the oxide surface by complete charge transfer and hence the adsorption energies had significant dependence on the U-value. They stated that the U-value influences the quantitative adsorption energy data, as well as the qualitative thermodynamic reaction profile.

Many similar studies\textsuperscript{43, 52, 54, 59} have been conducted for CuO as well. One of the widely accepted work is by Nolan et al.\textsuperscript{43}, where the U-value of 7 eV was shown to be consistent to match bulk properties like magnetic moment and the band gap of CuO. Another study by Maimaiti et al.\textsuperscript{54} showed that the energetic preference of different vacancies (surface and subsurface) on CuO(111) was not influenced by U-value. Hence, they claimed that for CuO(111), the U-value of 7 eV described both, the electronic structure and reaction energetics correctly. It must be noted here that, although U-values did not alter the trend of energetic preference, it affected the energies of individual structures by different magnitudes. Song et al.\textsuperscript{59} studied the partial oxidation of propylene on CuO(111). They showed that U-value did not affect the adsorption energy of propylene and hence used the U-value of 4 eV (as predicted by Wang et al.\textsuperscript{52} against bulk redox energetics) for the entire oxidation reaction. It must be noted that the effect of U-value was evaluated only on the adsorption (physisorption) of propylene and not for the entire reaction.

The aforementioned literature on determining the U-value for TMOs has following limitations: (i) they investigated and focused only on bulk oxides without any consideration to surface chemistry and adsorbate-surface interactions during the course of the reaction. This was a result of the presumption that the U-value which described bulk properties correctly will predict the energetics of a surface chemical reaction correctly too. However, work done by Huang et al.\textsuperscript{55} to determine the influence of U-value on CO adsorption on Cerium oxide showed that the inclusion of the adsorbate-surface interaction and adsorption configurations in the DFT+U calculations lead to a better and relevant estimate of U-value in catalysis applications.
involving strongly correlated systems. (ii) DFT computed energy values were compared to the thermodynamic enthalpy data taken from standard thermodynamic tables which are non-surface specific and ignore the role and influence of active surfaces in the reaction chemistry (e.g., lattice oxygen binding strength on different facets of CuO will affect reaction enthalpy when lattice oxygen is consumed in the reaction via the Mars van Krevelan mechanism\textsuperscript{19,21}). (iii) When a catalytic surface is formed, the breaking of \( z \) symmetry of the bulk phase leads to surface strains, defects, and a different atomic coordination from the bulk. Hence, surface magnetic properties are expected to differ from those of the bulk phase. TMOs being strongly correlated systems, the total atomic spin represents the spin of an ion better than the individual electronic spin of the electrons\textsuperscript{60}. In literature, the effect of different magnetic spin ordering configurations on the surface reactivity has been overlooked. (iv) Along the reaction coordinate, the \( d \) band of the oxide becomes partially filled, and hence U-value may affect the computed adsorption energies differently. The underlying assumption that the same U-value being valid for two different oxidation states of the same transition metal might not be correct. (v) It is important to note that even when the reactant’s binding energy is weakly affected by the U-value (reactant being physisorbed, weakly interacting or involving no or limited charge transfer), the adsorption energies of reaction intermediates or products, which involve complete charge transfer, vacancy formation and/or consumption of oxygen, might be strongly dependent on U. Hence, it is important to carefully examine the nature of reaction on the oxide surface and choose a uniform U-value which represents reaction energetics for a TMO correctly.

**1.5. Scope and Organization of the paper**

Hence, for the reasons stated above, considering the influence of surface characteristics (surface saturation, the binding energy of the lattice oxygen, acid-base characteristics, etc.) on the catalytic activity of TMOs, it becomes crucial to determine the U-value based on surface
reactions, rather than using the bulk property-optimized U-value. In the present work, we investigate the dissociative chemisorption of H$_2$ on the CuO surface to determine the U-value for surface catalytic reactions on CuO, taking into account complex surface-adsorbate interactions. Adsorption energies are measured experimentally using chemisorption experiments, and experimental surface characterization techniques are used to identify adsorption configurations. The reaction mechanism leading to the experimentally determined adsorption configuration is investigated computationally, and a U-value that correctly described the entire reaction energetics and adsorption energies over the CuO surface is identified.

In section 2, we describe the computational and experimental methods used in the study, followed by CuO morphology and surface characterization results in section 3.1. In section 3.2, we present the rationale for choosing H$_2$ as a probe molecule and a model catalytic reduction reaction. In section 3.3, we present the experimental H$_2$ chemisorption energies on CuO and discuss the possible H$_2$ adsorption configurations as computed by DFT calculations in section 3.4. In section 3.5, we identify the equilibrium H$_2$ adsorption configuration along the reaction coordinate by performing in-situ IR analysis of CuO catalyzed reduction reaction. In section 3.6, we discuss the effect of U-value on the adsorption enthalpy and present the range of U-values that accurately estimate the experimental chemisorption energy for CuO catalyzed surface reactions. We summarize the conclusions from this work in section 4.

2. Computational and Experimental Methods

2.1 Computational Methods

All the calculations in the current work were performed using GGA$^{61}$ with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in VASP$^{62}$ (Vienna *ab initio* simulation package) with the periodic plane wave implementation within DFT$^{62-63}$. We use the
projector augmented-wave (PAW)\textsuperscript{64-65} scheme to describe the inner core-valance interaction with a plane wave cut-off energy of 450 eV. For integration over the Brillouin zone, we used k points sampling of 4x4x1 within the Monkhorst-pack scheme. Integration is performed using tetrahedron method with Blöchl corrections. We used a four-layer CuO(111) slab with top three layers allowed to be fully relaxed; the number of slab layers and the density of k point grids were chosen to ensure the adsorption energies were well converged within 0.01 eV with respect to the computational setup discussed here. A vacuum region of 12 Å was wide enough to avoid interactions between different slabs. To ensure a high level of accuracy, energy convergence criteria of 10\textsuperscript{-6} eV per unit cell along with a minimization of interatomic forces to 0.01 eV/A was employed. Since CuO is antiferromagnetic at its ground state, we turned on spin polarization for all simulations involving CuO.

In the current DFT+U benchmarking study, in order to eliminate the effect of different lattice parameters on reaction energetics, and keep the computational system in close match to the experimental system, we fixed the lattice constants to the as obtained with U-value of 7 eV, as it showed excellent agreement with experimental lattice parameters (a, b, c, β), interatomic distances\textsuperscript{43} and reproduced experimental band gaps and magnetic moments\textsuperscript{42}. CuO has a monoclinic structure, and we have used the lattice constants a = 4.68 Å, b = 3.43 Å, c = 5.14 Å, β = 99.3\textdegree, as optimized by Varghese et al.\textsuperscript{21} with the above-mentioned U-value. All the calculations have been done on CuO(111) as it is the most stable CuO facet followed by CuO(-111)\textsuperscript{66}. Both CuO(111) and CuO(-111) have similar geometric configuration and surface structure arrangement of Cu and O atoms. CuO(111) facet has been predominantly found in our as-synthesized sample of CuO, which is used for experiments in this work.

CuO(111) surface has a repeating arrangement of O\textsubscript{3}-Cu\textsubscript{3}-O\textsubscript{4}-Cu\textsubscript{4} units (Figure 1a), where the subscript denotes the coordination number of the individual atom. Although CuO is antiferromagnetic, different atomic magnetic spin configurations are possible while
maintaining the antiferromagnetic behavior, such as line-by-line ordering (Figure 1a, where alternate rows of Cu atoms have opposite magnetic spins) and bulk-like magnetic ordering (Figure 1b, where alternate atoms of Cu in any particular row have opposite magnetic spins). Line-by-line magnetic spin ordering has been used in the current work. As per literature, the bulk-like magnetic ordering (Figure 1b) was only marginally stable than the line-by-line ordering (Figure 1a) by ~ 0.01 J/m², and both these magnetic orderings co-exist in a system. We also evaluated their effect on adsorption energies, and the calculated adsorption energies were unaffected by the change in these two magnetic order configurations.

We determined the zero-point energy (ZPE) and entropic and enthalpic temperature corrections for gas phase molecules from thermodynamic tables and for adsorbed structures as per statistical thermodynamics, where molecular partition function describes each of these effects. For the adsorbed species, these effects arise only from the vibrational motion of the adsorbed atoms hence we ignored the effects resulting from translational and rotational partition function. We expected the enthalpic contribution from the surface (clean or adsorbed) to be insignificant as compared to the adsorbate and did not include them in the vibrational analysis. In cases where the lattice oxygen dashed out of the surface and constituted a part of the adsorbed species or product, we no longer exclude its enthalpic contribution and evaluated it as a part of adsorbed species. We performed the frequency analysis with finite difference approximations with a displacement size of 0.01 Å, where atoms were individually displaced in each of the Cartesian direction.

Adsorption energy, \( E_{ads} \), was calculated as follows, for a model adsorption reaction:

\[
A(g) + \rightarrow A^* \tag{2}
\]

Using the expression,

\[
E_{ads} = E_{A^*} - (E_\ast + E_{A(g)}) \tag{3}
\]
\( E^* \) is the total energy of the system, \( E_s \) is the energy of the clean surface, and \( E_A(g) \) is the energy of the isolated gas phase molecule \( A(g) \). Since these energies are computed at 0 K, we added the ZPE and enthalpy temperature corrections \([H(T) - H(0)]\) to the computed reaction energies, as proposed by Irikura\(^6\), to compare the computational adsorption energies with the experimental enthalpy data. The surface coverage in the simulation is comparable to the experimental system. The net enthalpy of a reaction was calculated by

\[
\Delta H = \Delta E_{\text{Reaction}} + \Delta\{ZPE + [H(T) - H(0)]\}_{\text{Reaction}}
\]

(4)

2.2 Experimental Methods

CuO nanomaterial was synthesized by the precipitation method using NaOH solution as the precipitant. The concentrated NaOH solution, around 4M, was added dropwise to the \( \text{Cu(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O} \) solution under continuous stirring at room temperature. The black precipitate appeared as soon as the basic solution was added. The resultant slurry was aged under stirring at ambient temperature for 5 h, and the final product was collected by vacuum filtration, washed with deionized water, dried at 60 °C and calcined at 350 °C for 4 hours.

Experiments to investigate the water evolution (possibly due to hydrogen chemisorption followed by CuO reduction) were carried out using a continuous fixed bed reactor under Temperature Programmed Surface Reaction (TPSR) mode and products were monitored with a HPR 20 QMS Sampling System (Hiden Analytical). During TPSR test, a low-temperature ramping rate of 5 °C/min was used and the dwelling time is 10 min at each temperature.

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer under ambient temperature using CuK\(\alpha\) radiation operated at 40 kV and 40 mA in the 2θ range of 10°–80°, using a 0.05° step size of and a step time of 20 seconds at each point.
The morphology of the calcined catalyst was analyzed using a Field-emission scanning electron microscope (FE-SEM, Jeol JSM-6700) at an accelerating voltage of 5 kV. Further morphological information was acquired through transmission electron microscopy (TEM) observation using Tecnai G² TF20 S-twin microscopy operated at 200 kV. Samples were dispersed on carbon grids after sonicating the samples in ethanol for half an hour.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded on a Bio-Rad FT-IR3000 MX spectrometer equipped with a Harrick Praying Mantis DRIFTS cell connected to a liquid N₂ cooled mercury-cadmium-telluride (MCT) detector and a resolution of 4 cm⁻¹ with an accumulation of 64 scans in a single measurement. The catalyst was loaded into the reaction cell, and the reaction gasses were passed through the sample at a controlled flow rate. The background was recorded under Helium atmosphere at the reaction temperature. Background subtractions were performed for all spectra reported in the investigation.

Chemisorption was carried out with a Micromeritics ASAP 2020C instrument through static measurement of H₂ chemisorption. The heat of adsorption was calculated from the isosteric curves using Clausius-Clapeyron equation (Equation 5), a function of system pressure and the temperature.

\[
\Delta H^\circ_{\text{adsorption}} = R \left[ \frac{\partial (\ln P)}{\partial (1/T)} \right]_\theta
\]  (5)

3 Results and Discussion

3.1 CuO morphology and surface characterization

The as-synthesized CuO was characterized using XRD (Figure 2), and all the peaks in the spectra were representative of the monoclinic C/2c symmetry of cupric oxide. The morphology of CuO nanoparticles was examined by SEM and TEM (Figure 3) and the particles
had a cylindrical morphology, resembling nano-pellets. HRTEM was conducted and focused on different areas of the pellet surface, and we typically observed lattice fringes with a d spacing of 0.23 nm corresponding to the (111) plane as the most exposed surface in the as-prepared CuO. The same surface is used to model reactions in the computational work.

3.2 Choice of probe molecule and model reduction reaction

Most of the catalytic applications of CuO, such as partial and complete oxidation and dehydrogenation of hydrocarbons (and oxygen containing moieties) involve hydrogen abstraction, leading to both, the formation of adsorbed hydrogen species and the reduction of CuO. Hence, in this contribution, hydrogen was used as a probe molecule.

A typical hydrogen reduction reaction on a metal oxide can be broken down into the following elementary steps (Equations 6-9),

\[ \text{H}_2(g) + * \rightarrow \text{H}_2^* \]  
\[ \text{H}_2^* + * \rightarrow 2\text{H}^* \]  
\[ \text{Cu}_n\text{O}_n + 2\text{H}^* \rightarrow \text{Cu}_n\text{O}_{n-1} + (\text{H} - \text{O}_{\text{Lattice}} - \text{H})^* + * \]  
\[ \text{Cu}_n\text{O}_{n-1} + (\text{H} - \text{O}_{\text{Lattice}} - \text{H})^* \rightarrow \text{Cu}_n\text{O}_{n-1} + \text{H}_2\text{O}_{\text{Lattice}}(g) + * \]  

, where * denotes the various active surface sites. The elementary reaction steps are (i) \( \text{H}_2 \) adsorption on the surface to form molecularly adsorbed \( \text{H}_2^* \) (Equation 6), (ii) dissociation of \( \text{H}_2 \) to form different adsorbed \( \text{H}^* \) species (on surface metal or lattice oxygen centers) (Equation 7), (iii) reaction with surface hydroxyl species to form adsorbed \( (\text{H}-\text{O}_{\text{Lattice}}-\text{H})^* \) species (Equation 8) (iv) desorption of \( \text{H}_2\text{O} \), leaving the surface with one less oxygen per molecule of \( \text{H}_2 \) adsorbed (Equation 9).

3.3 Experimental adsorption energy measurements
The H\textsubscript{2} adsorption energy on CuO was experimentally measured using chemisorption method. Prior to the measurements, mass spectrometry (MS) based TPR (CuO with H\textsubscript{2}) was carried out to ensure that temperatures used for the chemisorption study won’t lead to the loss of CuO reduction products, i.e., water. (Equation 9). The results showed H\textsubscript{2}O peak evolution from 70 °C onwards, and hence we chose the temperature range of 30-50° C for chemisorption studies. The enthalpy values for H\textsubscript{2} adsorption on the as-synthesized CuO was observed to be 42.2-60.8 kJ mol\textsuperscript{-1}, as summarized in Table 1.

This adsorption enthalpy could correspond to any of the surface species that are present during the adsorption reaction (Equations 6-8). Hence, to accurately compare the above experimental adsorption enthalpies to DFT calculated adsorption energies, it was important to identify the equilibrium surface species and adsorption configurations along the course of the reaction.

3.4 Theoretically predicted adsorption configurations

We performed DFT calculations to evaluate different possible surface adsorption configurations along the course of the reaction and noticed that H\textsubscript{2} preferred to dissociatively chemisorb on the CuO surface, which was also observed by Bersani et al.\textsuperscript{69}. Due to the possibility of H\textsubscript{2} dissociation on different active sites of CuO(111) (Figure 1), dissociated hydrogens, \(H^*\), can occupy different adsorption configurations, as shown in Figure 4; (i) under-coordinated surface Cu\textsubscript{3} sites (Figure 4a), (ii) under-coordinated surface Cu\textsubscript{3}-O\textsubscript{3} pair sites (Figure 4b), (iii) under-coordinated surface O\textsubscript{3} sites, forming 2 hydroxyl species involving lattice oxygen \(H_{\text{lattice}}^*\) (Figure 4c), (iv) under-coordinated surface O\textsubscript{3} site, forming water-like structure involving lattice oxygen \((H-O_{\text{lattice}}-H)^*\) (Figure 4d). Since the under-coordinated surface sites are the active sites of the CuO surface\textsuperscript{19,21}, we did not evaluate the H\textsubscript{2} dissociation products on the less active surface sites (saturated Cu\textsubscript{4} and O\textsubscript{4} surface sites).
An initial free energy calculation at reaction temperatures for the aforementioned four configurations rendered H₂ dissociation on two Cu₃ atoms (Figure 4a) and between Cu₃-O₃ atoms (Figure 4b) to be unfavorable irrespective of the U value chosen. Hence, only two of the H₂ adsorption configurations (Figure 4c and 4d) were possible on the CuO (111) surface.

It is interesting to note that in the \((H-O_{Lattice}-H)^*\) configuration (Figure 5), the lattice O atom gets pulled out from the surface by 2 Å, leaving a surface vacancy. Similar structures were also found by Maimaiti et al⁵⁴ and Bersani et al⁶⁹. The formed water-like structure has the O-H bond lengths of 0.973 and 1.022 Å and HOH bond angle of 107.62°, as compared to a free gas phase water molecule with O-H bond lengths of 0.974 Å and HOH bond angle of 104.45°. These bond distances and angles did not change significantly for different U values.

3.5 Surface species characterization using DRIFTS

As discussed above, the dissociation of H₂ leads to various possible adsorption configurations, and to identify the adsorbed surface species along the reaction coordinate, we carried out the in situ DRIFTS analysis of H₂ reaction with CuO surface at the chemisorption temperature of 40 °C. The IR spectra were recorded at successive time intervals to gauge the evolution of various surface O-H species, and we observed that the reaction proceeds with the instantaneous evolution of a sharp peak (3595 cm⁻¹) in the O-H Stretching region, which was getting saturated at reaction time of 4 minutes, as shown in figure 6. The other O-H stretching peaks at 3629 cm⁻¹ and 3500 cm⁻¹ (broad) started to develop at 4 minutes and continued to grow as the reaction proceeded. The wide band in the H-O-H bending region (1450-1650 cm⁻¹) began to evolve slowly and did not saturate even after 27 minutes of the reaction. This confirmed the presence of H-O-H bond in the equilibrium adsorption configuration⁷⁰-⁷².

To comment on the evolution of adsorption configurations and establish the IR spectra peak numbers to corresponding O-H bonds, an associated FTIR study consisting of two experiments
was performed: (i) the activation of CH$_4$ on CuO, and (ii) the adsorption and splitting of H$_2$O on CuO.

In (i), methane was passed over dry CuO surface at the 300° C, which is high enough to activate the first C-H bond with energy barriers$^{21}$ of 76.6 kJ mol$^{-1}$, as per the following reaction:

$$\text{CH}_4 + 2 \ast \rightarrow \text{CH}_3 \ast + \text{H}_2\text{O} \ast$$  \hspace{1cm} (10)

* denotes the active surface site and $H_{\text{latticeO}}^*$ denotes the hydrogen from C-H cleavage that is adsorbed on the O$_3$ site. An important point to note here is that even though the methyl species can further oxidize, each subsequent C-H activation will also lead to more $H_{\text{latticeO}}^*$ species. Hence, the $H_{\text{latticeO}}^*$ formed as the product of this reaction should be the predominant -OH species in the system at this temperature. This is consistent with the IR results as shown in Figure 7a, where only one sharp O-H stretching peak was observed in the O-H stretching region at 3595 cm$^{-1}$, suggesting the splitting of methane C-H bond, as shown in equation 10.

In (ii), dry helium was purged through a pre-moisturized CuO surface to remove any gas phase moisture and retain only the surface adsorbed H$_2$O. This sample was then heated at a temperature of 300°C, to initiate water splitting as per the following reaction:

$$2 \ast + \text{H}_2\text{O} \rightarrow (OH)_{\text{Cu}}^* + H_{\text{latticeO}}^*$$  \hspace{1cm} (11)

, where * denotes the active surface site, $(OH)_{\text{Cu}}^*$ denotes the OH species (where the oxygen is from the split water) adsorbed on the surface Cu$_3$ site and $H_{\text{latticeO}}^*$ denotes the hydrogen from split water that is adsorbed on lattice O$_3$ site. IR spectra as shown in Figure 7b clearly presented two sharp O-H stretching peaks ($\approx$3595 cm$^{-1}$ and $\approx$3650 cm$^{-1}$) and one broad O-H stretching peak (which corresponds to the hydrogen bonded -OH species$^{72}$).

By having common OH species in the products (Equation 10 and 11) and comparing the IR spectra (Figure 7a and 7b), we can confirm that the sharp peaks at 3595 cm$^{-1}$ and 3650 cm$^{-1}$ correspond to $H_{\text{latticeO}}^*$ and $(OH)_{\text{Cu site}}^*$ species respectively. We applied the above insights
about the frequencies of various O-H peaks and the corresponding surface species, to understand the IR spectrum of the H₂ reaction on CuO (Figure 6) and conclude that:

(i) Instantaneous evolution of sharp peak at 3595 cm⁻¹ \((H_{\text{lattice0}}^*)\) established H₂ being dissociatively chemisorbed over two different lattice oxygens (figure 4c) as the first adsorption configuration.

(ii) The broad band in the H-O-H bending region (1450-1650 cm⁻¹) confirmed the presence of H-O-H bond in the equilibrium adsorption configuration and established the \((H-O_{\text{lattice}}^*)\) configuration (figure 4d) as the equilibrium adsorption configuration. O-H stretching peaks at 3500 cm⁻¹ (broad) and 3629 cm⁻¹ correspond to the stretching vibrations of two O-H bonds of \((H-O_{\text{lattice}}^*)\) configuration.

Based on the above, we proposed that the H₂ adsorption is a series reaction with \(H_{\text{lattice0}}^*\) (Figure 4c) being the first intermediate and \((H-O_{\text{lattice}}^*)\) configuration (Figure 4d) being the equilibrium adsorption configuration.

3.6 Comparison of experimentally measured and DFT+U calculated adsorption enthalpies

We performed DFT+U calculations for the adsorption of H₂ with systematic increments in U, to calculate the adsorption energy for both, the intermediate \(H_{\text{lattice0}}^*\) and equilibrium adsorption configuration \((H-O_{\text{lattice}}^*)\) on the surface and added the ZPE and enthalpy temperature correction factors to determine the enthalpy of adsorption. The influence of U-value on computed adsorption enthalpies is reported in Figure 8. The calculated adsorption enthalpy differed by 40 kJ mol⁻¹ & 100 kJ mol⁻¹ (for the same range of U-values) for the intermediate (Figure 8a) and for the equilibrium (Figure 8b) configuration, respectively. The comparison of DFT+U calculated adsorption enthalpies to experimental chemisorption enthalpies is shown in Figure 9, and we observed that the U-value of 4.5-5.5 eV correctly estimates the experimental adsorption enthalpy. The influence of U-value on
adsorption enthalpies is ascribed to the increase in electron localization with an increase in the onsite potential U. With more localization of electrons, their transfer between the surface and adsorbate is restricted, hence weaker adsorption is observed with each incremental U-value. Hydrogen chemisorption energy has been reported and accepted to be a suitable descriptor for the reactivity of metal oxide mediated hydrogen abstraction reactions in hydrocarbons73-77. Hence, due to the existence of this linear correlation between the activation barrier and H chemisorption energy, we suggest that the above determined U value, 4.5 – 5.5 eV (based on hydrogen adsorption enthalpies) would be appropriate to investigate hydrocarbon activation and oxidation on CuO too.

The bulk property optimized U-value of 7 eV which is widely used to model catalytic reactions over CuO, underestimated the experimental adsorption energies by 30 kJ mol⁻¹ (Figure 9) and thus failed to predict the correct reaction energetics and adsorption energies. This underestimation of adsorption energies by U-value of 7 eV was a direct result of the over-localization of valence d-electrons due to the application of a larger U-value than required. It is a common practice to determine the U-value for a system in a semi-empirical way, through seeking agreement with available experimental measurements of certain bulk properties or bulk redox energies and using these bulk determined U values to evaluate surface reactions and energetics. We showed that the bulk determined U-value and the U-value that determined the correct surface reaction energetics are different.

To determine the effect of U value on the desorption reaction, we calculated the desorption energy (equation 9) for the (H-O_{lattice}-H)* configuration for the U-value of 5 and 7 eV and quantified that the choice of U-value does not affect the desorption energy, as shown in Table 2. This signifies that once the lattice oxygen has been consumed in the reaction, leaving a reduced (partially or fully) surface, the influence of the U value on the reaction energy is not significant. Hence, U value of 5 eV (from the range 4.5-5.5 eV) should be used for the entire
surface catalytic reaction over CuO (111) surface. Hence, further emphasizing that the choice of U value (4.5-5.5 eV) not only replicates the adsorption energies but is able to correctly describe entire reaction energetics, including product desorption.

To investigate H-H lateral interaction and the effect of U value on it, we systematically increased hydrogen coverage in the first adsorption configuration ($H_{\text{lattice}}^*$) and observed that lateral interactions are insignificant up to 4 chemisorbed hydrogens in the unit cell. The effect of lateral interactions with the complete coverage of hydrogens on active O3 sites (6 hydrogen atoms) is also only 7% of the total energy. We also observed that these lateral interaction energies do not change with the change in U value.

The above work compares theoretical and experimental adsorption energies along with surface-adsorbate interactions with respect to different adsorption configurations on different surface-active sites. The U value range presented in the article is benchmarked with PBE exchange correlation functional and does not change significantly with the addition of van der Waals corrections (long-range interactions between the adsorbate and transition metal oxide surface). The presented U value range correctly accounts for the excessive electronic delocalization in CuO catalyzed surface reactions, independent of the vdw interactions. Hence, this U value should, in principle, be valid for reactions where van der Waals interactions may affect reaction energies, although a separate benchmarking for choosing the correct vdw corrections to DFT functional may still be needed in such a case. This DFT+U benchmarking procedure covers the entire reaction coordinate from reactant chemisorption and splitting, surface species reaction, vacancy formation and product desorption. It includes the effects of different magnetic spin ordering configurations, the participation of lattice oxygen in the reaction, the surface reduction and change in oxidation state of surface atoms due to the vacancy and product formation. It provides a method to determine a U-value which is valid for the entire reaction over a TMO surface.
4. Summary and Conclusions

The present work is a DFT+U benchmarking study for surface catalytic reactions over CuO surface, using H₂ as a probe molecule, combined with chemisorption experiments and surface and reaction species characterization using FTIR technique. CuO nano-pellets are synthesized using precipitation method with CuO(111) surface as the most exposed facet. The experimental H₂ adsorption enthalpy on as-synthesized CuO is observed to be 42.2-60.8 kJ mol⁻¹. Adsorption (dissociative) configurations along the reaction coordinate are determined by performing in-situ infrared analysis at adsorption temperatures. The systematic variation of U for DFT+U calculations shows that the U-value influences H₂ adsorption enthalpies up to 100 kJ mol⁻¹ for different adsorption configurations. For the IR validated equilibrium configuration, we compare calculated adsorption enthalpies with the experimental enthalpy of adsorption and conclude that a U-value of 4.5-5.5 eV correctly estimates the adsorption energetics. We also show that the U-value of 7 eV, as determined by fitting against various bulk properties of CuO, is an overestimation of the introduced energy penalty and leads to an underestimation of the adsorption energy. Although the benchmarking method uses H₂ as a probe molecule, the evaluated U value can be employed to other hydrocarbon based surface catalytic reactions over CuO(111). This work establishes a benchmarking procedure that encompasses the effect of various surface-adsorbate interactions (dissociation, chemisorption, and desorption) and a dynamic surface environment to present a surface specific approach to determine the U-value for TMO catalyzed reactions. This method can be applied to determine the appropriate U-value for other TMOs using a suitable choice of the probe molecule and experimental data to model and simulate their catalytic surface reactions accurately.

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REFERENCES


FIGURES.

Figure 1. The surface atomic arrangement on CuO(111) facet showing the repeating arrangement of \(\text{O}_3\)-\(\text{Cu}_3\)-\(\text{O}_4\)-\(\text{Cu}_4\) units, where the subscript denotes the coordination number of the respective atom. a) Line-by-line magnetic spin ordering (where the alternate rows of Cu atoms have opposite magnetic spins) b) Bulk-like magnetic spin ordering (where the alternate atoms of Cu in any particular row have opposite magnetic spins). The upward and downward arrows represent the positive and negative spin respectively. Peach and red balls represent Copper (Cu) and Oxygen (O) atoms, respectively.
Figure 2. X-ray diffractograms of as-synthesized CuO with signature peaks of copper (II) oxide.
Figure 3. Morphology characterization of the as-synthesized CuO a) SEM image depicting the nano-pellets morphology b) Bright field TEM image with HRTEM image insert for the nano-pellets depicting lattice fringes corresponding to the (111) facet.
Figure 4. Different possible surface adsorption configurations for H$_2$ adsorption on CuO (111), where the two dissociated hydrogen atoms, $H^*$, occupy a) two under-coordinated surface Cu$_3$ sites, b) under-coordinated surface Cu$_3$-O$_3$ pair sites, c) under-coordinated surface O$_3$ sites, forming two hydroxyl species involving lattice oxygen $H^{*}_{lattice0}$ d) under-coordinated surface O$_3$ site, forming water-like structure involving lattice oxygen ($H$-$O_{lattice}$-$H^*$). Peach, red and white balls represent Copper (Cu), Oxygen (O) and Hydrogen (H) atoms respectively.
**Figure 5.** Surface adsorption configuration for H\textsubscript{2} adsorption on CuO, where the two dissociated hydrogen atoms, H\textsuperscript{*} occupy a single lattice oxygen, forming (H-O\textsubscript{lattice}-H)* configuration with Cu-O bond length of 2.00 Å and, the O-H bond lengths of 0.973 and 1.022 Å and HOH bond angle of 107.62°. Color code is the same as Figure 4.
Figure 6. In-situ DRIFT spectra at consecutive time intervals for $\text{H}_2$ (5% $\text{H}_2$/95% Ar) adsorption on CuO at a constant temperature of 40°C, shows a) O-H bond stretching region and b) H-O-H bond bending region. Symbols: (*) 3595 cm$^{-1}$; (#) 3629 cm$^{-1}$; (♦) 3500 cm$^{-1}$
Figure 7. DRIFT spectra for (a) activation of CH₄ on as-synthesized CuO and b) adsorption and splitting of H₂O on as-synthesized CuO. Symbols: (*) 3595 cm⁻¹; (●) 3650 cm⁻¹; (♦) 3250 cm⁻¹.
Figure 8. Variation of adsorption enthalpy with incremental U-values for DFT+U calculations for a) \(H^*_{\text{latticeo}}\), intermediate adsorption configuration and b) \((H-O_{\text{lattice}}-H)^*\) equilibrium adsorption configuration for H\(_2\) adsorption on CuO.
Figure 9. Comparison of DFT calculated adsorption enthalpies for the equilibrium configuration to the experimental adsorption enthalpies.
TABLES

**Table 1.** Enthalpy of H$_2$ adsorption (kJ mol$^{-1}$) for different adsorption coverages (Quantity of H$_2$ adsorbed per gram of CuO), as calculated using isosteric adsorption curves to solve Equation 5.

<table>
<thead>
<tr>
<th>Quantity of H$_2$ gas adsorbed (cm$^3$/g STP)</th>
<th>Enthalpy of adsorption (kJ mol$^{-1}$)</th>
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Table 2. Desorption energy (kJ mol$^{-1}$) of ($H$-$O_{lattice}$-$H$)* adsorption configuration forming gas phase water for different U values.

<table>
<thead>
<tr>
<th>U Value (eV)</th>
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</tr>
<tr>
<td>7</td>
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