Mechanistic *ab-initio* DFT Study of CO_2 Hydrogenation to olefines on $MgH_2(001)$

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Resumo/Abstract

RESUMO - Apresentamos uma investigação teórica abrangente sobre o processo de hidrogenação do CO_2 na superfície de $MgH_2(001)$, com foco no papel do hidrogênio (bulk) como fonte primária de H. Nossos resultados revelam uma via de reação que envolve a formação espontânea de formato (*HCOO) após a adsorção de CO_2, seguida pela hidrogenação para intermediários dioxometileno (*H_2COO) e hidroximetoxi (*H_2COOH). Em condições pobres em H_2, intermediários C1 parcialmente hidrogenados podem sofrer acoplamento para formar produtos C2 com seletividade para olefinas. Este trabalho fornece insights fundamentais sobre a catálise mediada por MgH_2 e estabelece um caminho para o *design* racional de catalisadores de hidreto metálico capazes de converter seletivamente o CO_2 em condições limitadas por H_2.
Palavras-chave: CO_2, hidrogenação, olefinas, hidretos metálicos, catálise computacional.

ABSTRACT - We present a comprehensive theoretical investigation of CO_2 hydrogenation on the $MgH_2(001)$ surface, focusing on the unique role of lattice hydrogen as the primary H source. Our findings reveal a distinct reaction pathway involving spontaneous formate (*HCOO) formation upon CO_2 adsorption, followed by subsequent hydrogenation to dioxomethylene (*H_2COO) and hydroxymethoxy (*H_2COOH) intermediates. Under H_2-lean conditions, partially hydrogenated C_1 intermediates can undergo coupling to form C_2 products with selectivity toward olefins. This work provides fundamental insights into hydride-mediated catalysis and establishes a mechanistic framework for rational design of metal hydride catalysts capable of selective CO_2 conversion under H_2-limited conditions.

Keywords: CO_2, hydrogenation, olefins, metal hydrides, computational catalysis.

Introduction

The catalytic hydrogenation of CO_2 to olefins is a major focus of carbon utilization research. Some mechanistic routes for CO_2 hydrogenation to olefins exist, including, e.g., the Fischer–Tropsch (FT)–like route and the methanol-mediated route [1]. Several catalysts have been investigated, e.g., Fe- and zeolite-based catalysts, oxides, boron and C-based materials, single-atom catalysts, perovskites, MOF-derived catalysts [2-6]. In this context, metal hydrides offer a different perspective as they can deliver H atoms stored as lattice (bulk) H^- species. For example, MgH_2 have been shown to hydrogenate CO_2 to C_2–C_4 olefins with high selectivity under low H_2/CO_2 ratio or even without H_2[7,8]. Notwithstanding the potential advantages, the detailed mechanism on pure MgH_2 surfaces is not fully established. Key questions include how CO_2 adsorb and activate, what are the stable intermediates and the energetics for each hydrogenation step.

By uncovering the mechanistic details of CO_2 hydrogenation to olefins on the $MgH_2(001)$ surface, this study holds broader implications for the design and optimization of hydride-based catalysts in general. In fact, we contribute with fundamental insights into how a hydride phase interact with CO_2 and facilitate subsequent C–H and C–C bond formation. Such insights are crucial for understanding how bulk H atoms may participate in catalytic reactions, especially under H_2-lean conditions or even in its absence. Such knowledge is not only critical for improving the catalytic performance of known materials but also for guiding the rational design of new metal hydrides or mixed hydride systems with tailored activity and selectivity. Cost-effective alternatives to traditional catalysts such as the one developed here serve as a valuable foundation for advancing a new generation of hydrogenation catalysts with tunable activity and selectivity toward high-value products like olefins.

In this work, we address these issues via first-principles DFT calculations and perform a systematic mechanistic study of CO_2 hydrogenation on the $MgH_2(001)$ surface using lattice hydrogen as the H source.

Methodology

All theoretical calculations employed periodic plane-wave DFT as implemented in Quantum ESPRESSO (QE). The PBE exchange–correlation functional was used, along with an empirical van der Waals correction (DFT-D2) to

account for dispersion interactions, as implemented in QE [9]. PAW pseudopotentials were used for Mg, H, C, and O and all calculations were performed considering spin polarization. Kohn-Sham electronic valence states were expanded in plane-waves up to 50 Ry and 400 Ry for kinetic energy and charge density cutoff, respectively. Brillouin-zone integrations used a 2×2×1 Monkhorst–Pack grid to ensure energy convergence. All structures were relaxed until forces were below than 1×10^{-3} Ry/Bohr and the variation of the total energy between two consecutive iterations was on the order of 1×10^{-4} Ry.

The MgH_2(001) surface was modeled by a periodic slab with a vacuum of ~15 Å to avoid interactions between periodic images. We considered the (001) surface because it offers more accessible adsorption sites and can be more representative under catalytic conditions. Lattice parameters were taken from bulk optimization and the 6-layer slab thickness was chosen to converge surface properties and a (2×2) surface unit cell was used to allow enough separation between; we compared the total energy of systems calculated with finer k-mesh and one extra layer, which produced only small changes in the adsorption energy and no appreciable changes in the geometric, therefore, the results reported here suggest that the chosen theoretical method is adequate and the results are reliable.. CO_2 adsorption and reaction steps were modeled by placing the molecule at various sites/orientations on the relaxed clean surface (Figure 1). We explicitly modeled H atoms as being abstracted from the slab: each hydrogenation step corresponds to a transfer of a H atom to the adsorbed species. Transition states (TS) for H atom transfers were located using the climbing-image nudged elastic band method and confirmed through vibrational frequency calculations, determined through the DFPT as implemented QE. The local minima and transition states were validated by none or single imaginary frequency, respectively, corresponding to the expected reaction coordinate. In a few cases, small residual imaginary modes (always below 100i cm^{-1}) persisted despite extensive optimization efforts. These modes are attributed to rigid-layer movements of the fixed atoms of the slab and do not involve any reactive motion; thus, they were deemed irrelevant to the reaction mechanism and were ignored. Accordingly, infrared (IR) spectra were simulated by computing vibrational frequencies and intensities for each intermediate; these spectroscopic signatures provide valuable benchmarks for experimental validation of the proposed reaction intermediates.

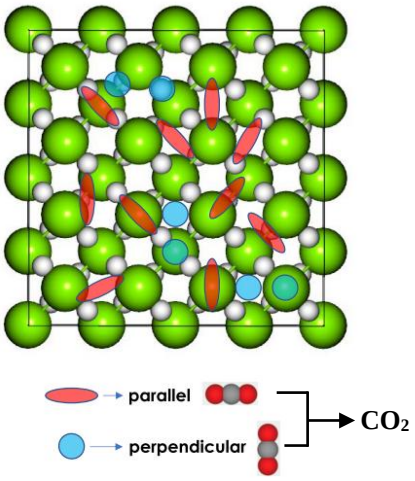

Figure 1 – Initial adsorption positions for CO_2 adsorption on the MgH_2(001) surface. Color code: green, Mg; white, H; gray, C; red, O.

Results and Discussion

We first examined CO_2 adsorption on the clean MgH_2(001) surface and two main orientations were tested (CO_2 parallel to the surface and perpendicular), including several initial positions (Figure 1). As the molecule is electrophilic at the C center, the presence of hydride species in MgH_2 would facilitate the activation. In principle, the first hydrogenation could proceed via two competing routes, i.e., formation of formate (*HCOO) or carboxyl (*COOH) intermediates. However, our calculations revealed that the adsorption is highly exothermic (E_{ads} = -2.31 eV) and leads to the spontaneous formation of a formate species (*HCOO). This process involves the transfer of a surface H to the C atom of CO_2, effectively achieving the first hydrogenation step without an activation barrier. In the optimized geometry, C is bonded to a H atom while both O atoms remain coordinated to surface Mg sites. The C-H bond length in the formate is 1.09 Å, consistent with a typical C-H single bond, while the two C-O bonds measure 1.27 Å and 1.25 Å, indicating partial double-bond character distributed across the O-C-O geometry. The spontaneous formation of *HCOO can be attributed to the strong nucleophilic character of the surface hydride species in MgH_2. This might represent a significant advantage of hydride-based catalysts, as they can activate CO_2 under mild conditions without requiring additional activation steps. The calculated vibrational frequencies for the adsorbed formate species reveal characteristic IR signatures that could serve as experimental benchmarks. These include an asymmetric O–C–O stretching mode at 1578 cm^{-1}, a symmetric O–C–O stretching at 1347 cm^{-1}, and a C–H stretching mode at ~2950 cm^{-1} (Figure 2). These calculated frequencies are in

good agreement with experimental IR data for formate species on various oxide surfaces [10], providing confidence in our computational approach.

Following the formation of formate (*HCOO), we explored two possible pathways for the second hydrogenation step: (1) addition of a H atom to one of the O atoms, forming adsorbed formic acid (*HCOOH), or (2) addition of hydrogen to the C atom, yielding dioxomethylene (*H_2COO). Our calculations indicate that the direct protonation of *HCOO to form *HCOOH has a substantial energy barrier (E_a = 2.70 eV) and is endothermic by +1.18 eV. The high barrier can be attributed to the unfavorable electrostatic interaction between the negatively charged hydride and the partially negative O atom. In contrast, the transfer of a second surface hydride to the carbon atom to form *H_2COO proceeds with a much lower barrier (E_a = 0.80 eV) and is exothermic by -1.15 eV. This significant difference in activation energies and reaction energetics indicates that the *HCOO → *H_2COO pathway is strongly favored kinetically and thermodynamically. The optimized structure of the *H_2COO intermediate shows a nearly tetragonal geometry around the carbon atom, with two C-H bonds (1.10 Å) and coordination of both oxygen atoms to surface Mg sites. The calculated IR spectrum for *H_2COO (Figure 2) shows distinctive features: C-O stretching modes near 1000-1100 cm^{-1} and C–H stretching vibrations around 2800-2900 cm^{-1}, slightly shifted from those of the formate precursor.

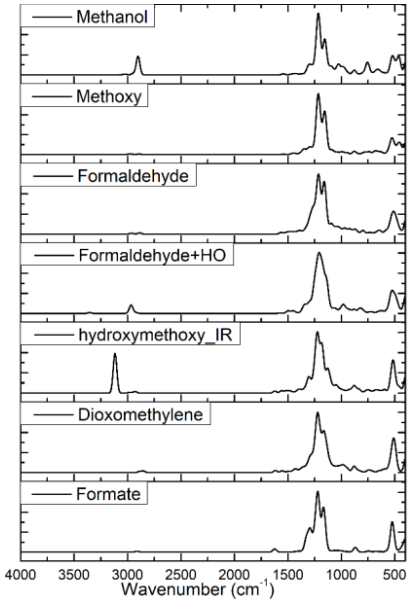

Figure 2 – DFT simulated IR spectra of the CO_2 hydrogenation intermediates.

We also explored an alternative pathway for ***HCOO** conversion, involving its cleavage into ***HCO** and ***OH** fragments. This process has a higher barrier (E_a = 1.90 eV) and is endothermic by +0.72 eV, making it less favorable than the direct hydrogenation to ***H_2COO**. This finding suggests that the reaction preferentially proceeds through intact C_1 intermediates rather than fragmenting into smaller units at this stage.

Thus, the next hydrogenation step involves the conversion of ***H_2COO** to hydroxymethoxy (***H_2COOH**) by adding a H atom to one of the O atoms. Our calculations show that this process has a relatively high activation barrier (E_a = 2.57 eV) and is endothermic (ΔE = +2.03 eV), identifying it as the rate-limiting step; the full potential energy surface is shown in Figure 3. The transition state for this step involves a rearrangement of the surface species to facilitate the approach of a lattice hydride to the partially negative O atom and the high barrier is consistent this rearrangement. In the optimized ***H_2COOH** structure, one O atom forms a hydroxyl group (O-H bond length: 0.94 Å) while the other remains coordinated to a surface Mg site. The calculated IR spectrum for ***H_2COOH** features a characteristic O-H stretching mode at 3450 cm^{-1}, confirming the formation of a hydroxyl group. Additional spectral features include C-O stretching vibrations at 1050-1200 cm^{-1} and C-H stretching modes at approximately 2850-2900 cm^{-1}.

Once ***H_2COOH** is formed, the next crucial step involves C-O bond cleavage to eliminate water and form surface-bound formaldehyde (***H_2CO**). Our calculations indicate that this dehydration process has a relatively high activation energy (E_a = 1.28 eV) and is exothermic (ΔE = -2.20 eV). The transition state for this step involves an elongation of the C-O bond and partial transfer of the hydroxyl H atom to a nearby surface site. The resulting ***H_2CO** intermediate adopts a tilted geometry on the surface, with the C atom coordinated to a surface Mg site and the O atom positioned away from the surface. The C=O bond length (1.25 Å) is consistent with the double-bond character expected for formaldehyde. The calculated IR spectrum for ***H_2CO** retains the C-H stretching modes at 2800-2900 cm^{-1} and exhibits a C=O stretching vibration at approximately 1720 cm^{-1}, characteristic of carbonyl compounds.

The adsorbed formaldehyde (***H_2CO**) can undergo further hydrogenation through the addition of a lattice hydride to the carbonyl carbon, forming a methoxy species (***CH_3O**). Our calculations show that this step is slightly highly exothermic (ΔE = -0.10 eV) with an activation barrier of 2.32 eV. The energy release reflects the conversion of a C=O double bond to C-O, coupled with the formation of a new C-H bond. In the optimized ***CH_3O** structure, the carbon atom adopts an approximately tetrahedral geometry, with three C-H bonds (1.09-1.10 Å) and a C-O bond (1.42 Å) that connects the methyl group to the surface through an O bridge. The calculated IR spectrum for ***CH_3O** displays weak C-H stretching vibrations at 2800-2900 cm^{-1} and lacks the O-H stretching band, consistent with a methoxy rather than a methanol species.

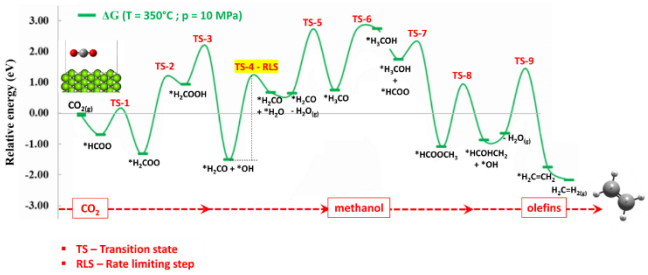

Figure 3: Calculated potential free-energy surface for hydrogenation of CO_2 to ethylene.

The final hydrogenation step in this pathway involves the addition of another hydride to the oxygen atom of *CH_3O, resulting in the formation of adsorbed methanol (*CH_3OH). This step has a substantial barrier (E_a = 2.15 eV) and is endothermic (ΔE = +1.87 eV), reflecting the stable nature of the methoxy species on the surface. The optimized structure of *CH_3OH shows a typical methanol geometry, with the hydroxyl O coordinates to a surface Mg site. The calculated IR spectrum would display the characteristic O-H stretching mode at approximately 3650 cm^{-1}, along with C-H stretching vibrations at 2850-2950 cm^{-1} and a C-O stretching mode at approximately 1030 cm^{-1}. Overall, our calculations indicate that methanol emerges as a key product of the reaction between CO_2 and four lattice hydrogen atoms on MgH_2(001). However, the high barrier for the final hydrogenation step suggests that the methoxy intermediate (*CH_3O) may accumulate on the surface under certain conditions, potentially leading to alternative reaction pathways or even leading to the formation of CH_4.

C-C coupling and olefin formation - A particularly interesting aspect of CO_2 hydrogenation on MgH_2 is the observed selectivity toward olefins, especially under conditions of limited hydride availability (no gas-phase H_2 or even low H_2/CO_2 ratios). To understand this phenomenon, we investigated potential C-C coupling pathways involving the partially hydrogenated C_1 intermediates identified in our study. The full mechanism is illustrated in Figure 4. Our calculations suggest that under conditions where surface hydride concentration is diminished, partially hydrogenated species such as formaldehyde (*H_2CO) or methoxy (*CH_3O) can undergo coupling reactions to form C-C bonds. For example, adjacent methanol and formate molecules can couple to form an adsorbed methyl-formate intermediate (*$HCOOCH_3$), which can subsequently dehydrate to form ethylene (C_2H_4).

In fact, we examined the energetics of the coupling reaction between two adjacent *HCOO species. The second *HCOO was formed spontaneously upon the adsorption of an extra CO_2 (E_{ads} = -1.19 eV). Regarding the C-C coupling, it was found a moderate activation barrier (E_a = 1.65 eV) for this process. This barrier is lower than those for the complete hydrogenation pathway to methane, suggesting that C-C coupling becomes competitive when hydride availability is limited. The formation of olefins through these coupling pathways is consistent with experimental observations showing increased selectivity at higher temperatures (which mobilize lattice hydrogen) and under low H_2/CO_2 ratio conditions [4-8]. In effect, low hydride concentration inhibits complete hydrogenation to methane, leaving unsaturated or partially saturated fragments available for C-C coupling reactions. The calculated potential energy surface for these coupling reactions implies a viable pathway from methanol (or related intermediates) to olefin precursors: a C-C bond forms followed by dehydrogenation steps to yield ethylene. This mechanism explains the observed selectivity patterns and provides insights for tuning reaction conditions to favor olefin production [7,8].

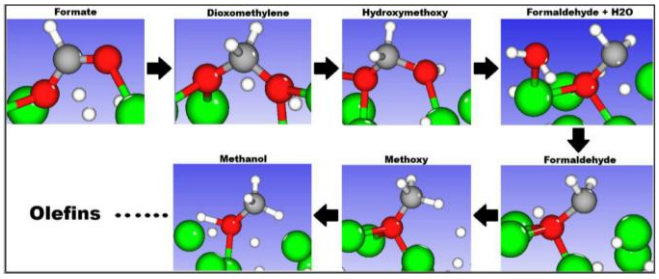

Figure 4 – Sequência de etapas elementares proposta para hidrogenação de CO_2 sobre MgH_2. Color code: green, Mg; White, H; gray, C; red, O.

These findings highlight the dynamic nature of the MgH_2 catalyst under reaction conditions and suggest that the catalyst evolves as the reaction progresses. The initial high activity for CO_2 activation can be attributed to the abundance of reactive hydride species, while the selectivity toward olefins at later stages may be linked to the emergence of defect-rich, partially dehydrogenated regions that facilitate C-C coupling. Overall, this study demonstrates that pure MgH_2(001) can mediate CO_2 hydrogenation via lattice H atom to form formate and beyond, and it clarifies the sequence of elementary steps and their energetics.

Conclusions

A Our findings provide valuable insights into the mechanism of CO_2 hydrogenation to olefins on the MgH_2(001) surface using lattice hydrogen. These insights have several important implications for the design and optimization of hydride-based catalysts for CO_2 conversion.

First, our results highlight the critical role of the MgH_2 surface structure and its H content in the catalytic process. Engineering the surface by introducing, e.g., other metal atoms could potentially tune the availability of lattice hydrogen and the adsorption strength of CO_2 and reaction intermediates, thereby influencing the activation barriers and overall reaction rates. Second, maintaining a sufficient supply of lattice H atom is crucial for sustained catalytic activity. Thus, strategies such as operating under moderate pressures of H_2 to replenish the lattice hydrogen or employing co-catalysts (e.g., Cu or Ni nanoparticles dispersed on the surface) could facilitate H_2 activation and spillover onto the MgH_2 support effectively maintaining the hydride reservoir. Third, our findings confirm that pure MgH_2 alone exhibit limited conversions due to the relatively high barriers for certain steps. Therefore, a synergistic approach involving the coupling of MgH_2 with other elements could enhance their activity and selectivity.

Future work should include kinetic modeling of the reaction network (using the computed barriers) to predict turnover frequencies and selectivities under reaction conditions. Also, experimental validation via, for instance, in-situ IR/DRIFTS would be valuable to observe the predicted bands. Finally, exploring other hydride materials (LiH, CaH_2, NaH) or hydride composites could expand the scope in CO_2 conversion. Tailoring the hydride composition and support (e.g. MgH_2 on some support) might optimize the balance between H atom donation and intermediate stabilization. Despite this promising potential, it is important to mention that hydrides are usually difficult materials to work with, so the experimental conditions must be tuned accordingly.

In summary, this work provides a comprehensive mechanistic framework for understanding CO_2 hydrogenation offering a roadmap for designing improved hydride-based catalysts for the selective conversion of CO_2 to olefins under H_2-limited conditions. By leveraging the unique chemistry of lattice hydrogen, these materials represent a promising approach to carbon utilization in a likely H_2 costly/constrained future.

Acknowledgements

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