DFT+U Study of Strain Engineered CO2 Reduction on a CeO2(110) Facet

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Resumo/Abstract

RESUMO - Foi realizada uma avaliação sistemática do impacto das vacâncias de oxigênio presentes na superfície do CeO2 em sua atividade de redução de CO2 através de cálculos periódicos da Teoria do Funcional da Densidade. Os cálculos revelaram que o CO2 adsorvido na superfície do CeO2 adota uma configuração em ponte, similar à espécie carbonato, para todas as superfícies de CeO2, independentemente da natureza e localização das vacâncias. Estas configurações de geometria foram utilizadas como reagentes para explorar a redução de CO2 em CO através de cálculos NEB (Nudged Elastic Band).

*Palavras-chave: Superfícies de CeO2, DFT, conversão de CO2, hidrocarbonetos*

ABSTRACT - Herein, a systematic assessment of the impact of oxygen vacancies present at the CeO2 surface on its CO2 reduction activity was performed by periodic Density Functional Theory calculations. These calculations firstly revealed that the adsorbed CO2 at the CeO2 surface initially adopts a preferentially bent configuration for all CeO2 surfaces invariant of the nature/location of the vacancies. These geometry-optimized configurations further served as starting points to explore CO2 reduction into CO via DFT-based Nudged Elastic Band calculations.

*Keywords: CeO*2 *surfaces, DFT, CO*2 *conversion, hydrocarbons*

## Introduction

Excessive emission of CO2 has emerged as an environmental challenge over the last few decades. This pressing issue calls for urgent exploration of efficient and cost-effective technologies aimed at mitigating atmospheric CO2 and suppressing the greenhouse effect. One promising approach for producing clean energy involves the conversion of CO2 into fuels like CH4, higher hydrocarbons and CH3OH. However, achieving a significant conversion through catalytic reactions remains a formidable obstacle due to the inherent thermal stability of CO2 against its initial reduction. Among the potential catalysts, ceria (CeO2) has garnered substantial attention for its viability in facilitating the initial CO2 reduction1. Herein, a systematic investigation of the impact of oxygen vacancy on CeO2 was investigated by periodic DFT calculations for the initial reduction of CO2. Among the ceria polymorphs, CeO2 (110) has been chosen owing to its remarkable catalytic property and stability.

## Methods

DFT calculations were performed by using the Vienna *ab initio* Simulation Package (VASP)2,3. The Perdew-Burke-Ernzerhof functional (PBE) is used for the exchange-correlation. Ionic cores are described by the projector augmented wave method (PAW) with a plane wave energy cutoff of 520 eV. The slab model of the ceria (110) surface was cleaved from the geometry-optimized bulk structure (lattice parameter of a = 5.41 Å), and the bottom two atomic layers of the five-layer slab are maintained fixed. A value of U = 4.5 eV was considered for the Ce 4f states. The Brillouin zones are sampled using a (3×2×1) Monkhorst-Pack grid.

## Results

The vacancy formation energy on the first layer of CeO2 (110) surface was calculated to be 44.0 kcal/mol. A similar value of oxygen vacancy formation energy was found by Cheng et al.4 Adsorbed CO2, with adsorption energy of -41.1 kcal/mol, on the neighboring site of the oxygen vacancy is activated into a bent configuration with <OCO = 123.9° (Figure 1a). The two symmetrical C−O bonds in the bent structure have lengths of 1.28 Å and 1.30 Å, and the C−O bond length in which the C atom interacts with the surface O atom of ceria is 1.33 Å. The energy required for the generation of oxygen vacancy in the second layer was 55.8 kcal/mol, in agreement with the value obtained by Pérez-Bailac et al.5 The CO2 molecule is adsorbed with binding energy of −59.8 kJ/mol, and bent configuration (with <OCO = 126.7° and C−O bond length of 1.28 Å), which is similar to the structure computed for the adsorption on the vacancy in the first layer (Figure 1b).

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**Figure 1.** Adsorbed configuration of reactant of CO2 conversion on surface ceria with vacancy (a) in the first layer and (b) in the second layer.

## Conclusions

The most stable adsorbed configurations are the bent structure of CO2. These configurations were used as starting points for the CO2 conversion to CO on ceria surfaces. The Nudged Elastic Band calculations are being performing to construct a reaction energy diagram for the mechanistic pathways for CO2 reduction to CO and hydrocarbons on CeO2 (110) surface.

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