Influence of Oxygen Vacancy in Ni-supported Ceria Nanorod Surface on CO_2 Methanation: Ab-initio Thermodynamics-based Study

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Highlights

- Ab-initio thermodynamics study is used to determine catalyst surface structure
- CO_2 Methanation likely to proceed through CO_2 dissociation on Ni-ceria interface followed by CO hydrogenation

1. Introduction

Carbon capture utilization and storage (CCUS) is a collection of various techniques in which CO_2 is captured and either stored or used to produce multiple other chemicals/fuels. Converting CO_2 to methane is one of the means to store renewable energy as it is a hydrogen carrier and a feedstock for other value-added chemicals. Experimental literature showed nickel supported on ceria nano-rod morphology with (110) as the primary facet is highly active and reasonably stable surface to support Ni for the reaction.[1] However reaction mechanism and the role of the different components in the catalyst in determining the reaction pathways and energetics is still not clear. This investigation is aimed at addressing this aspect using detailed Density Functional Theory simulations with ab-initio thermodynamics approach. This study will help to understand the behavior of CO_2 methanation reaction on ceria nanorod surface at atomic scale under typical CO_2 methanation reaction conditions.

2. Methods

Vienna Ab-initio Simulation Package (VASP) software is used with PBE exchange correlation functional & spin-polarized periodic DFT + U-based calculations. A plane-wave basis set with a kinetic energy cut-off of 450 eV is imposed for the expansion of valence electron states. The Hubbard U correction of 4.5 eV is imposed for 4f electronic states of Ce atoms, in accordance with previous literature.[2] Grimme's dispersion corrections (DFT-D3) are incorporated to account for the van der Waals forces associated. A periodic p(2x3) CeO2(110) supercell is modeled to represent the nanorod surface. Ni_4 cluster in tetrahedral coordination is supported on this surface to represent Ni-supported ceria catalyst. The model is subjected to ab-initio thermodynamics analysis to determine surface structure under typical CO_2 methanation conditions (T =200-300°C, P = 1 atm). Transition States of elementary reaction steps are estimated by Nudge Elastic Band (NEB) method and are confirmed by vibrational frequency analysis.

3. Results and discussion:

3.1. Catalyst Surface Structure under typical reaction conditions:

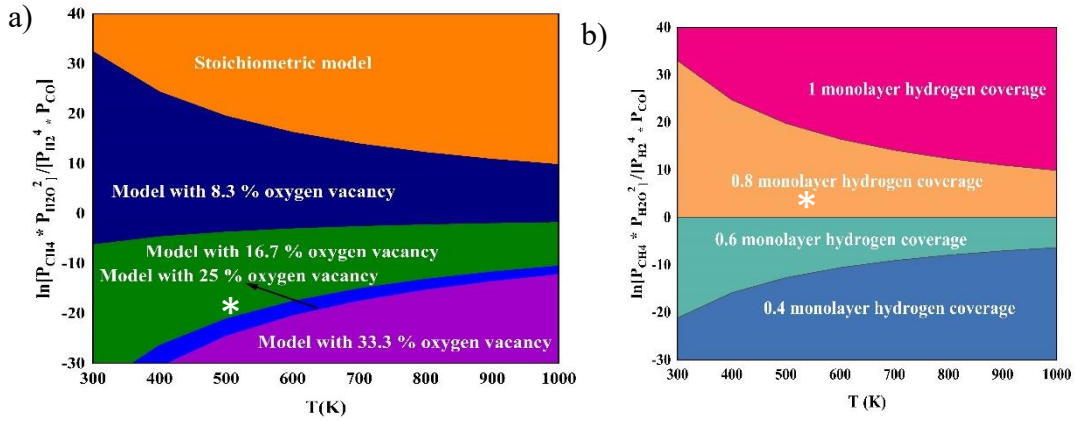

Figure 1:a) Surface Phase Equilibrium of different oxygen vacancy containing Ni_4/CeO_2 (110) catalyst surfaces, b) Surface Phase Equilibrium of surfaces with different hydrogen coverage. [(*) mark denotes typical CO_2 methanation reaction conditions(T = 200-300°C, P = 1 atm)

Figures 1a) & 1b) show catalyst surface structure after ab-initio thermodynamics study. The results show that 16.7% oxygen vacancy & 0.8 monolayer hydrogen coverage on $Ni_4/CeO_2(110)$ catalyst are thermodynamically stable under typical CO_2 methanation conditions (T = 200-300°C, P = 1 atm). That is denoted as "*" mark I figure 1a) & 1b).

3.2 CO_2 Methanation Pathway Analysis:

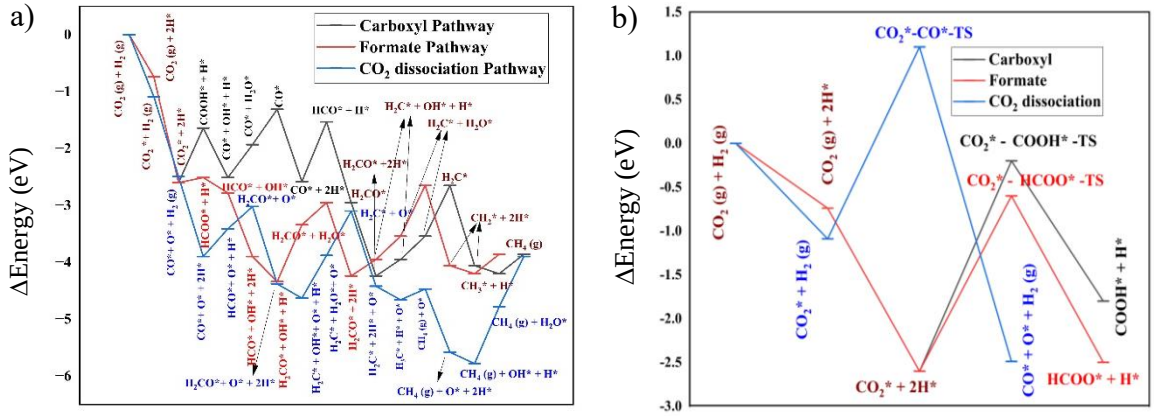

Figure 2: a) Potential Energy Diagram of CO_2 methanation on Ni_4/CeO_{2-x} (110) surface through different pathways with all intermediates, color codings: carboxyl pathway & corresponding intermediates – black, formate pathway & corresponding intermediates - red, Intermediates common to both – maroon, CO_2 dissociation pathway & intermediates – blue. b) Transition states for the first intermediates for all pathways;

From figure 2b), it is observed that CO_2 dissociation is highly exothermic (-1.40 eV) compared to HCOO formation (-0.1 eV) & COOH formation (0.8 eV). Activation barrier for HCOO formation from CO_2 is 2.1 eV while CO formation & COOH formation has barriers of 2.2 eV & 2.5 eV respectively. Water formation & desorption steps are endothermic in all the pathways with energy ranging from 0.8-1 eV. Due to high exothermicity of CO_2 dissociation coupled with similar energy barriers for first intermediates across all the pathways, CO_2 dissociation pathway seems to be the most favorable pathway for the methanation reaction. In the CO_2 dissociation pathway, CO_2 dissociates to form CO on Ni & the oxygen atoms fills one lattice oxygen vacancy near the Ni_4-$CeO_2(110)$ interface. CO undergoes successive hydrogenation to form HCO & H_2CO with reaction energy of 0.5 eV & 0.37 eV respectively.H_2CO species undergoes dissociation in presence of hydrogen to form H_2C with reaction energy of -0.25 eV. CH_2 undergoes successive hydrogenation to form CH_3 & CH_4 with reaction energy of -0.24 eV & 0.19 eV respectively. Finally, after CH_4 formation, water is desorbed from the catalyst surface by taking one oxygen from the lattice. In this way, oxygen vacancy is regenerated in the lattice.

4. Conclusions:

$Ni_4/CeO_2(110)$ catalyst with 16.7% oxygen vacancy concentration & 0.8 monolayer hydrogen coverage is thermodynamically favorable under operating conditions (T = 200-300°C, P = 1 atm). CO_2 methanation is likely to be initiated by direct dissociation of CO_2 to CO. This pathway is both kinetically and thermodynamically favorable compared to the formate & carboxyl pathways.

References:

[1] Y. Xie, ACS Catal, pp. 10587–10602, 2022
[2] A. P. Pushkar, J Catal, vol. 413, pp. 681–691, Sep. 2022.

Keywords
"Ab-initio Thermodynamics; Density Functional Theory; CO_2 Methanation; Oxygen Vacancy."