No coke, no problem: theoretical perspective on how visible light prevents carbon accumulation during DRM on nickel-ceria catalysts

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Highlights

- DRM on Ni-CeO_2 converts CH_4/CO_2 to CO-rich syngas but suffers from coking.
- Visible-light photothermocatalysis on Ni-CeO_2 prevents coking at 400–600 °C.
- TD-DFT was used to understand light-induced CeO_2 expansion and O mobility.
- Light-driven O spillover to Ni lowers barriers for carbon oxidation to CO.

1. Introduction

Methane dry reforming converts methane and carbon dioxide into syngas with a high CO content. The reaction is thermocatalytically carried out on nickel catalysts supported by ceria. Despite the excellent properties of nickel, practical application is hindered by extensive coking. Carbon accumulation on the catalyst decreases its activity and necessitates periodic regeneration.

A novel approach to prevent carbon build-up is to use light and heat as simultaneous energy sources. Under illumination, the reaction proceeds photothermocatalytically at nickel-ceria interfacial sites. In the excited states, new reaction channels open, and the mobility of active oxygen increases significantly. Our experiments show that illumination with visible light at an intensity of around 6 suns completely prevents coking when the reaction temperature is maintained at 400–600 °C. The origin of this phenomenon was poorly understood. Here, we report extensive quantum chemical calculations in both the ground and excited states, which were used to elucidate the behavior of the catalyst under illumination. Comprehensive structural, electronic, and mechanistic calculations were performed and compared with our experimental findings to provide a credible explanation for the superior performance under illuminated conditions. [1]

2. Methods

Calculations were performed using density functional theory (DFT) and time-dependent DFT (TD-DFT), as implemented in VASP. To compare performance under dark and light conditions, both DFT and TD-DFT simulations were conducted. The support was modeled as a CeO_2(111) slab, with the nickel active phase represented by a one-atom-thick adlayer of Ni atoms. For structural optimizations, the GGA functional (PBE) was used. Electronic properties were evaluated at a higher level of theory (HSE06). The equilibrium lattice constant was calculated under both dark and light conditions. In both scenarios, the mobility of oxygen atoms was investigated by determining the activation barrier for their surface and bulk diffusion. The entire reaction mechanism of DRM was studied on Ni/CeO_2 for surfaces under various lighting conditions. Finally, the effect of nickel atoms on absorption properties was examined.

3. Results and discussion

To distinguish photothermal effects from light-induced structural changes, we performed TD-DFT calculations on photoexcited Ni-CeO_2. By optimizing the ground and excited state structures, we observed approximately 0.6% lattice expansion in the excited state. Experimentally, nickel is required to achieve visible-light photoexcitation of ceria and the associated lattice expansion. Pristine, coarse-grained CeO_2 has a band gap of about 3.2 eV, which is above the visible range. Surface deposition of Ni both introduces active catalytic sites and narrows the band gap, enhancing visible-light absorption. Our modelling of a CeO_2(111) slab with increasing Ni coverage (0 to 1 monolayer) shows a monotonic increase in absorption with higher Ni loading.

Our calculations reveal two distinct contributions to illumination-enhanced oxygen mobility: lattice expansion and excited-state electronic effects. Oxygen migration on $CeO_2(111)$ is characterized by the activation energy for surface diffusion, which corresponds to hopping between neighboring Ce sites. As the lattice expands, this barrier decreases due to weakened O-Ce bonding, and TD-DFT shows an additional barrier reduction resulting purely from changes in the electronic structure, with a relative weight of approximately 3:1 (structural to electronic).

We next examined the energy landscape for methane dehydrogenation and subsequent carbon oxidation on Ni-CeO_2. The first C-H activation step ($CH_4 \rightarrow CH_3 + H$) has a significant barrier (~1.3 eV) and, along with carbon oxidation, forms the rate-determining manifold in DRM. Illumination has little impact on the energetics of the first three dehydrogenation steps or on CH oxidation ($CH + O \rightarrow CHO$). In contrast, the final dehydrogenation step shows a pronounced light effect, with the activation barrier lowered by approximately 0.2 eV and the reaction becoming about 0.3 eV more exothermic; stronger expansion further reduces the barriers. The subsequent C oxidation to CO retains an activation energy of about 1.8 eV and is only weakly affected by illumination. [2]

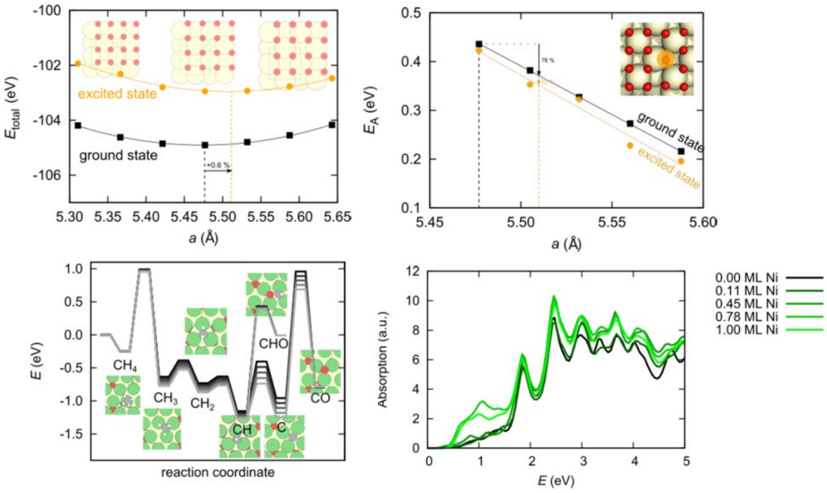

Figure 1. A) CeO_2 (111) Lattice expansion upon illumination, B) Mobility of oxygen atoms (activation energy) as a function of cell lattice constant under dark and illuminated conditions; C) Reaction energy profile for methane activation, carbon build-up and de-coking on Ni/CeO_2, and D) Absorption profiles for $CeO_2(111)$ with varying amounts of surface Ni.

4. Conclusions

Our combined TD-DFT and experimental study shows that visible light fundamentally alters Ni/CeO_2 behavior during DRM. Illumination induces CeO_2 lattice expansion and excited-state electronic changes, which strongly enhance oxygen mobility and spillover to Ni sites. Overall, the light-sensitive step in carbon gasification appears to be the facile migration of oxygen from ceria to Ni sites, enabling carbon removal as CO via highly mobile oxygen originating either from CO_2 dissociation on Ni or from lattice oxygen spillover. As a result, carbon formed during methane activation is rapidly oxidized to CO, preventing coke accumulation even at 400–600 °C under ~6-sun irradiation.

References

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[2] K. Lorber, V. Shvalya, D. Vengust, J. Zavašnik, M. Huš, A. Pavlišič, B. Likozar, M. Mazaj, P. Djinović, Visible light illumination unlocks oxygen diffusion within ceria and solves the carbon formation problem during methane dry reforming reaction, 2026, *submitted*.

Keywords

Methane dry reforming, TD-DFT, nickel, coking.