A DFT study for the selective hydrogen combustion against propylene hydrogenation on CeO_2, $ZrCeO_2$, $CaMnO_3$ and $LaMnO_3$ catalysts.

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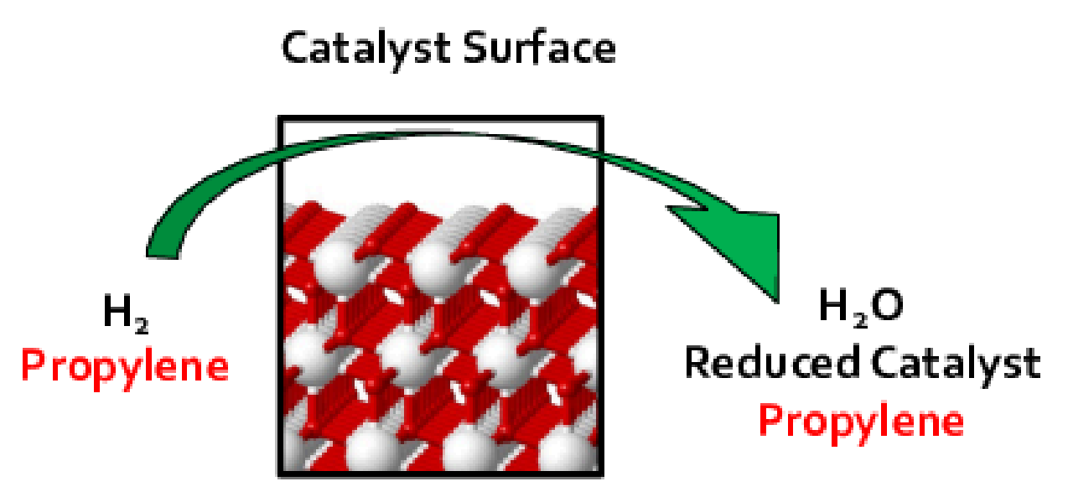
Introduction

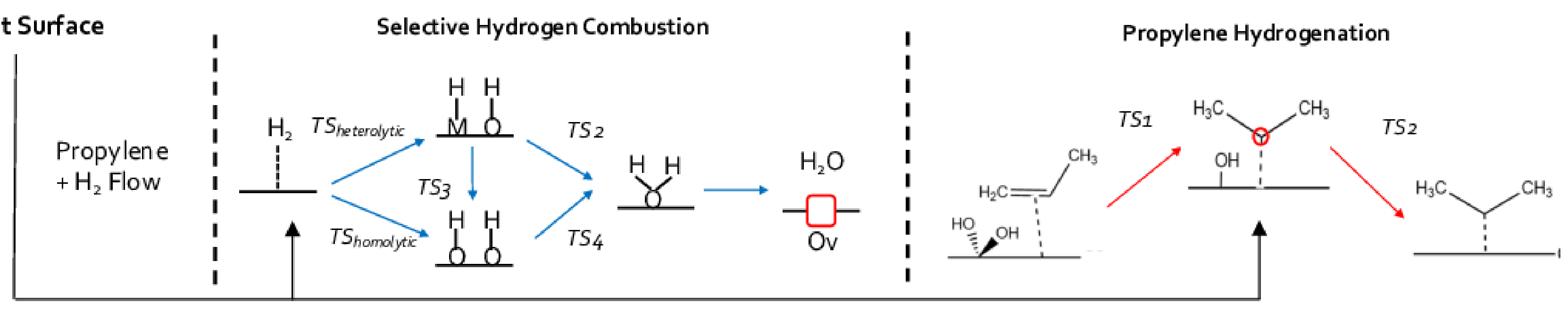
Present production of light olefins is based on the thermal or catalytic dehydrogenation of alkanes, but the reaction needs a high amount of energy to maintain conversion and to separate the H_2 and olefin products. The process can be separated into two steps, in which the first step (alkane dehydrogenation) produces olefin and H_2, and the second step (selective hydrogen combustion, SHC) transforms H_2 into H_2O through chemical looping process without converting the olefin, using a solid oxygen carrier (SOC) instead of O_2. A suitable SOC should have high oxygen storage capacity and fast H_2 combustion kinetics but also should be able to prevent olefin re-hydrogenation or overoxidation.

In this work we investigate by means of periodic DFT calculations the mechanism of SHC and undesired propylene hydrogenation on four different catalyst models: $CeO_2(111)$, $ZrCeO_2(111)$, LMO(110) and CMO(001) in order to understand their catalytic performance.

Aim

To study the capability of CeO_2, $ZrCeO_2$, CMO ($CaMnO_3$) and LMO ($LaMnO_3$) as SOC materials for the H_2 combustion reaction in the presence of propylene.

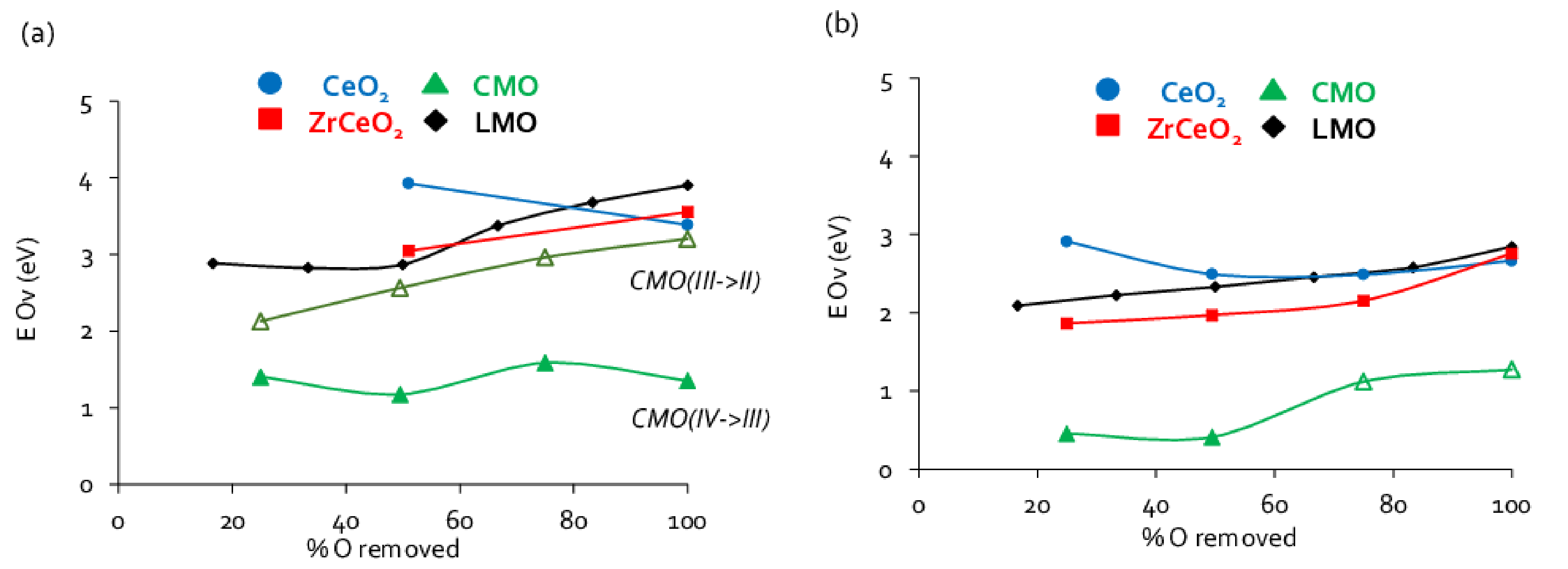




Reducibility of Materials

The formation of successive oxygen vacancy (Ov) defects was calculated optimizing atomic positions for surfaces and optimizing also cell parameters for bulk materials.

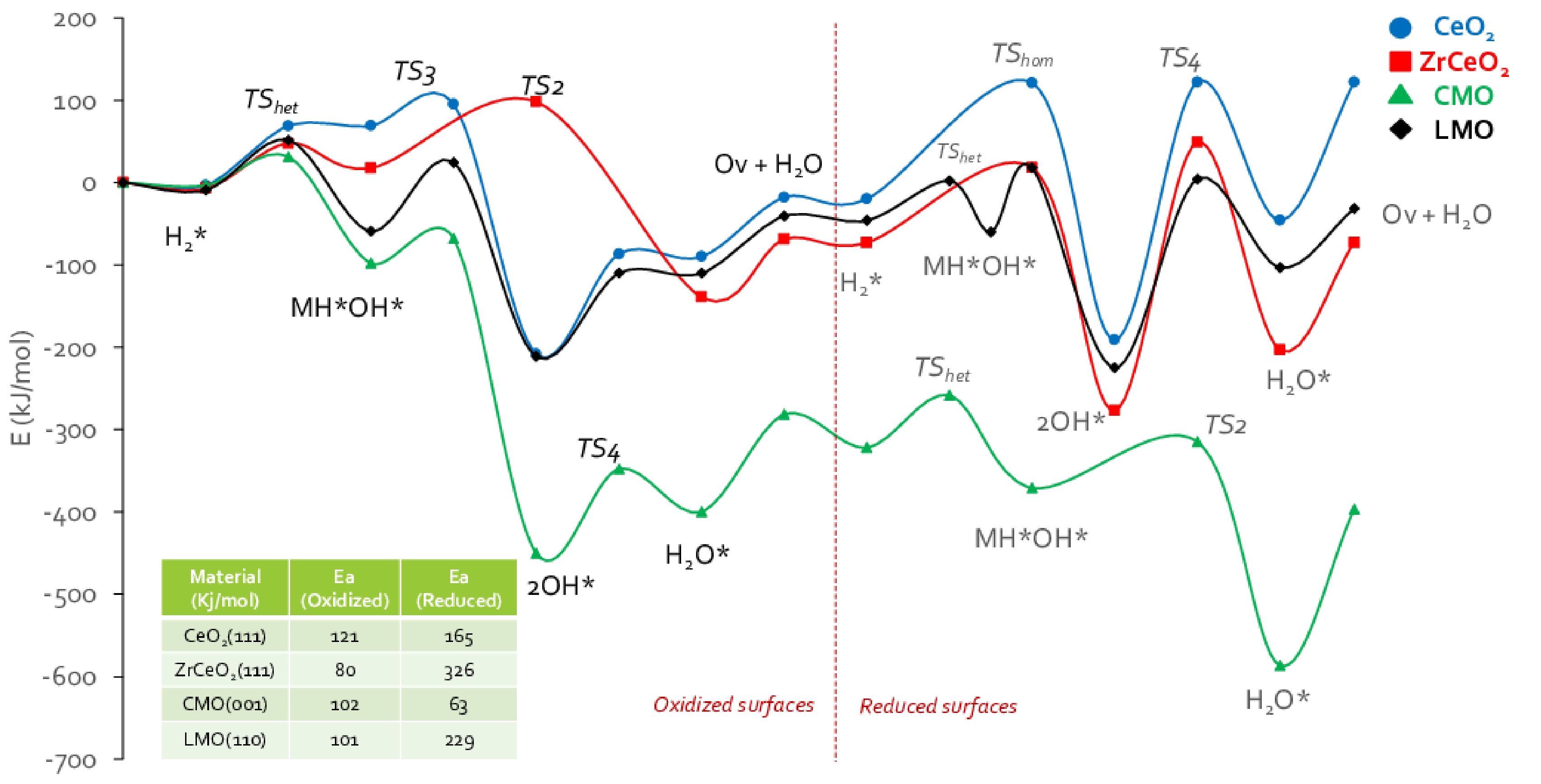
Oxygen vacancy formation energy (EOv) at increasing vacancy densities in (a) bulk solids and (b) most stable surfaces of materials.



H_2 Combustion: SOC + H_2 → SOC_Ov + H_2O

We have studied the mechanism of SHC process on oxidized and also on partially reduced surfaces. We found CMO as the most suitable material for the process due to his low activation energy in the overall path.

Energy profile on $CeO_2(111)$, $ZrCeO_2(111)$, CMO(001) and LMO(110) surfaces for the most favorable H2 combustion pathway.

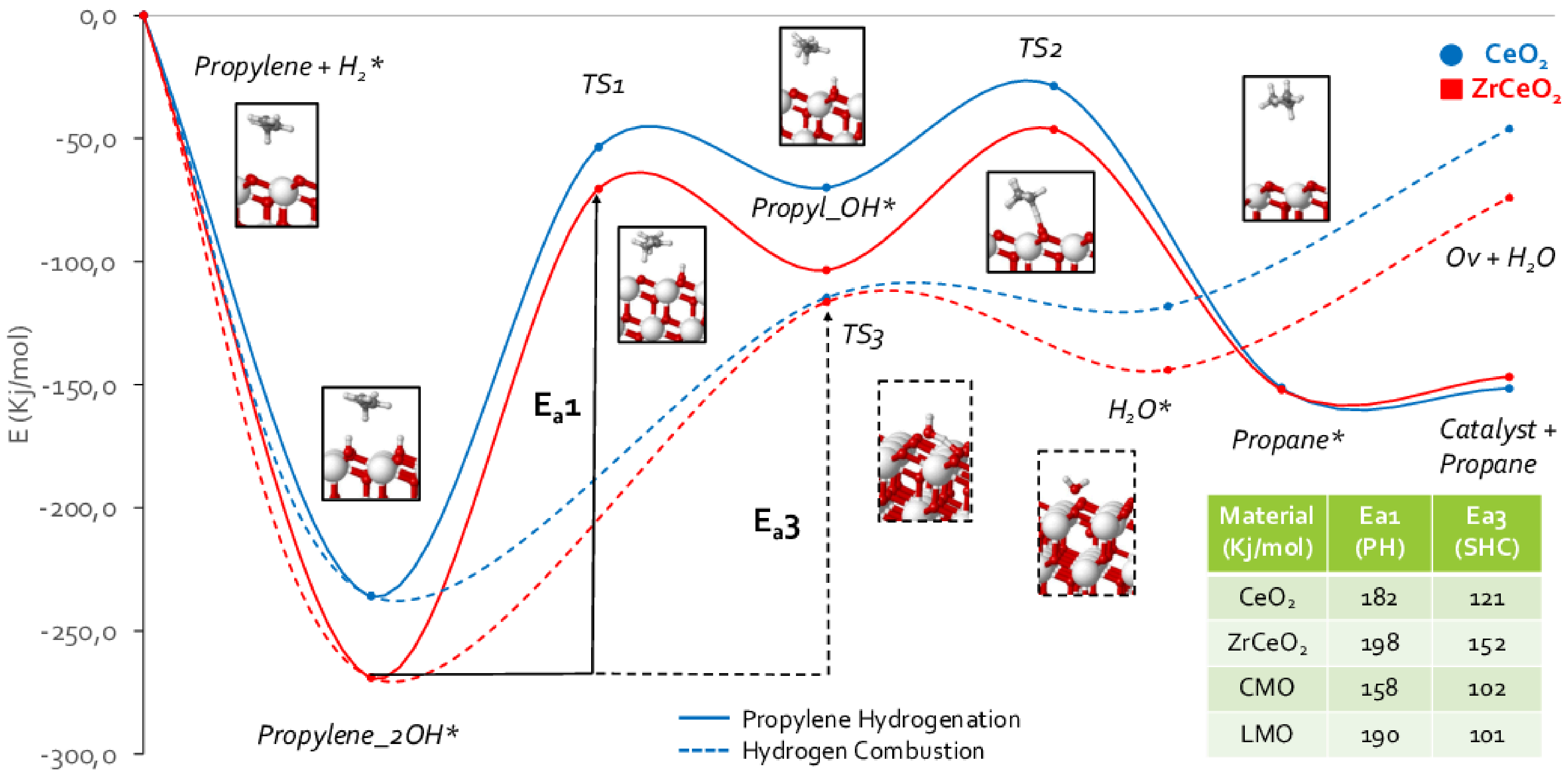


Material (Kj/mol)	Ea (Oxidized)	Ea (Reduced)
$CeO_2(111)$	121	165
$ZrCeO_2(111)$	80	326
CMO(001)	102	63
LMO(110)	101	229

Selectivity against Propylene Hydrogenation

H_2 can react with propylene to form propane or with the catalyst surface to form H_2O molecules. Comparing the activation energies for SHC and propane formation we found all the materials are selective for the combustion reaction.

Energy profile on $CeO_2(111)$, $ZrCeO_2(111)$ surfaces for the Selective Hydrogen Combustion reaction

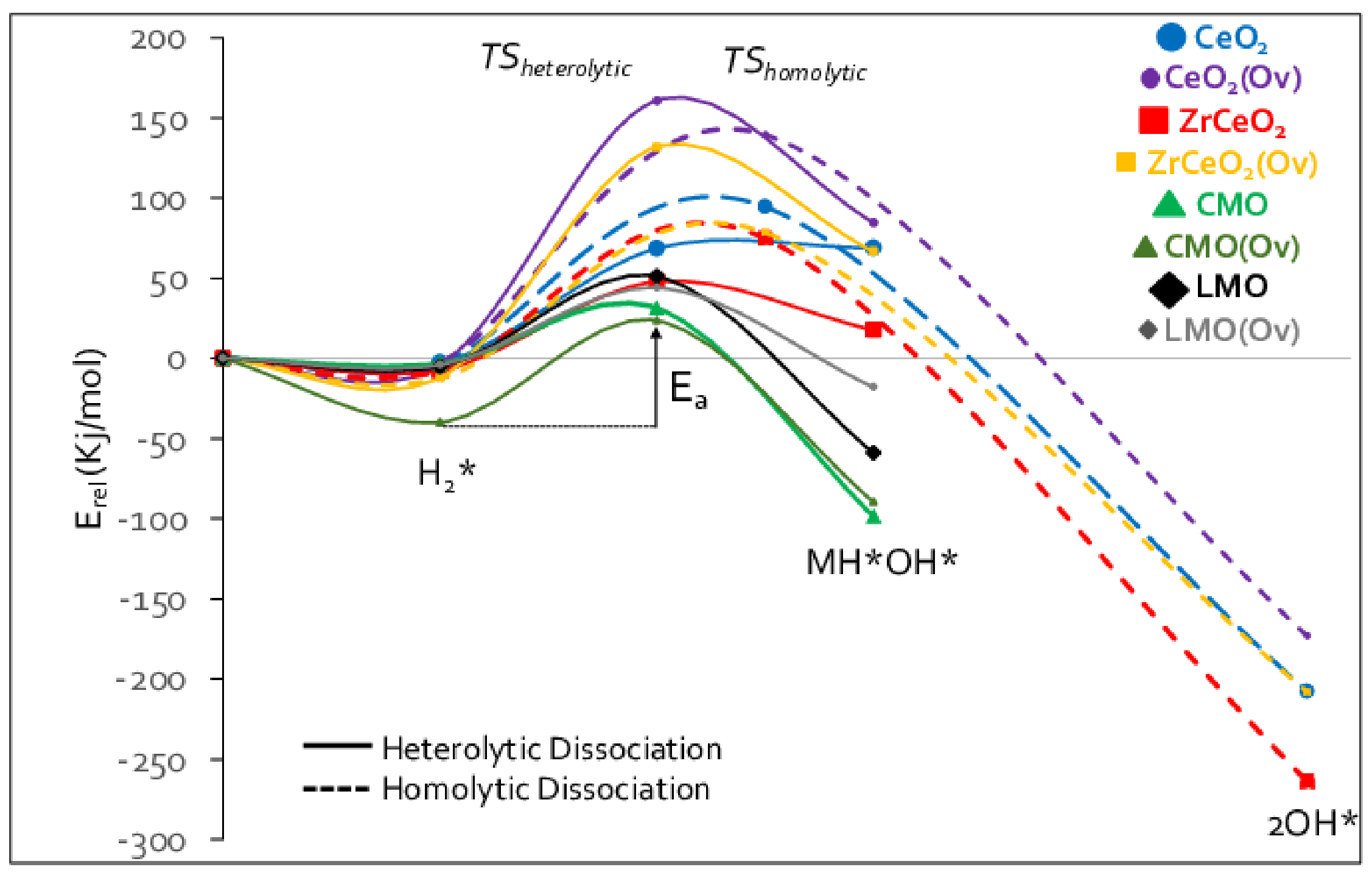


Material (Kj/mol)	Ea1 (PH)	Ea3 (SHC)
CeO_2	182	121
$ZrCeO_2$	198	152
CMO	158	102
LMO	190	101

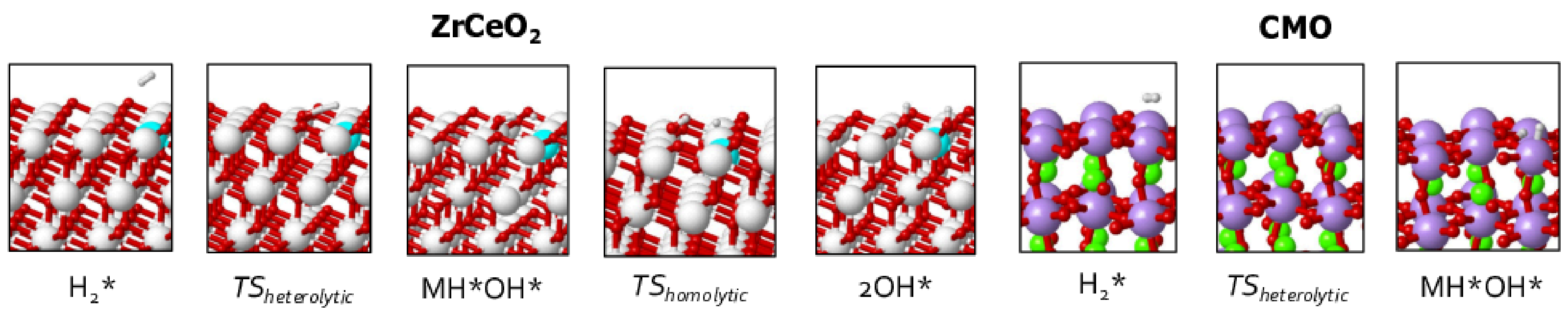
H_2 Dissociation: $H_2 \rightarrow H_2^* \rightarrow 2H^*$

H_2 dissociates heterolytically forming a M-H bond and a O-H bond on every material and also homolytically forming 2 O-H bonds on cerias. Heterolytic dissociation is more favorable on the oxidized surface and homolytic dissociation is favoured on the partly reduced surface for cerias.

Energy profile on $CeO_2(111)$, $ZrCeO_2(111)$, CMO(001) and LMO(110) surfaces



Material (Kj/mol)	Ea (Het)	Ea (Hom)
CeO_2	72	97
CeO_2(Ov)	165	142
$ZrCeO_2$	55	83
$ZrCeO_2$(Ov)	144	91
CMO(001)	34	---
CMO(001, Ov)	63	---
LMO(110)	61	---
LMO(110, Ov)	48	---



Computational Details

- Periodic DFT calculations were performed using PBE exchange correlation functional within GGA as implemented in VASP code.
- All calculations are spin polarized and the CUTOFF used is 420.0 eV for CeO_2 and $ZrCeO_2$ models, and 520.0 eV for CMO and LMO models.
- Every Bulk structure was generated from experimental structural data. The optimized unit cell parameters are a=b=c=5.47 Å for CeO_2; a=b=c=5.40 Å for $ZrCeO_2$; a=b=5.65 Å, c=13.52 Å for LMO; and a=5.32 Å, b=5.41 Å, c=7.56 Å for CMO.
- Slab models for $CeO_2(111)$, $ZrCeO_2(111)$, CMO(001) and LMO(110) were made with four atomic layers and ~ 25 Å of vacuum.

Conclusions

CMO perovskite is considerably easier to reduce than the rest of materials in the bulk material and in studied surfaces.

H_2 can be dissociated over every studied surface heterolytically and also homolytically on CeO_2 and $ZrCeO_2$. We have found CMO (001) as the most suitable material for H_2 dissociation through an heterolytic pathway and $ZrCeO_2$ (111) as the most favourable through an homolytic pathway.

Every material is able to complete the entire mechanism for the H_2 combustion reaction on studied surfaces, finding CMO as the most promising one.

CeO_2 and $ZrCeO_2$ are able to hydrogenate the propylene formed, but in both cases that process is not favored against the H_2 combustion reaction.

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