Mechanistic Understanding of the Formation of Dimethoxy Carbonate from the CO_2 Esterification with Methanol on the CeO_2 (111) Surface

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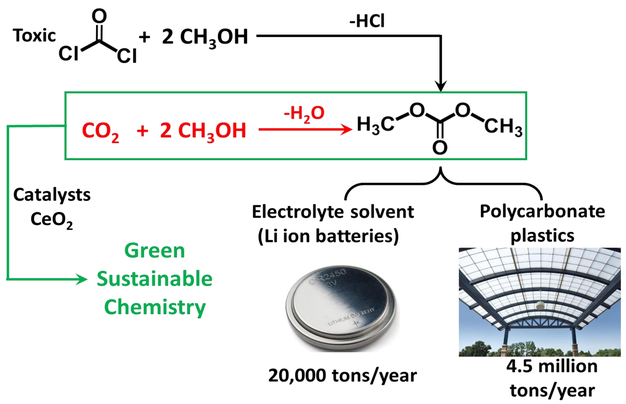
MOTIVATION



Advantages:

- Dimethyl carbonate (DMC) is the simplest but the most important organic carbonate in industry.
- In convention, DMC is produced by the phosgene method (the reaction route in black). Such method is far from 'green chemistry' due to the high toxicity of phosgene. Other alternative methods suffer from high energy cost.
- Instead, the direct synthesis of DMC from the esterification of CO_2 with methanol will be preferable from the viewpoint of the green chemistry and the low energy cost.
- Cerium oxide as a widely used heterogeneous catalyst has shown emerging potential as a green catalyst for the direct synthesis of DMC from CO_2 and methanol.

Challenges:

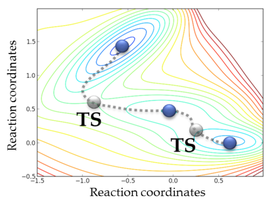
- The DMC yield from such method is still very low (~2%) due to the thermodynamic limitation if no third chemical is used .
- The reaction rate is also very low (take 25 h to reach 1.6% yield).
- To improve the performance of CeO_2 catalysts, it is indispensable to understand the catalytic mechanism at the atomic level.

OBJECTIVES

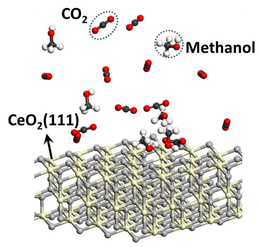
Use theoretical methods to explore the formation mechanism of DMC on the CeO_2 surface with or without oxygen vacancy

- Explore how CeO_2 catalyzes the formation of DMC
- Unravel the role of the oxygen vacancy
- Figure out the origin of the low rate of DMC on CeO_2

COMPUTATIONAL METHODS



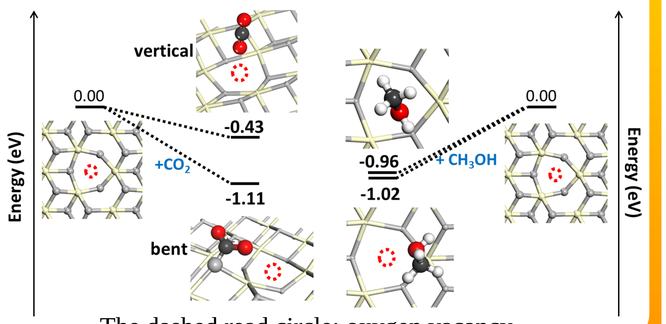
Climbing-image nudged elastic band (CI-NEB) method: Find transition state (TS).



Molecular dynamics (MD): Dynamic adsorption behaviors of CO_2 and methanol

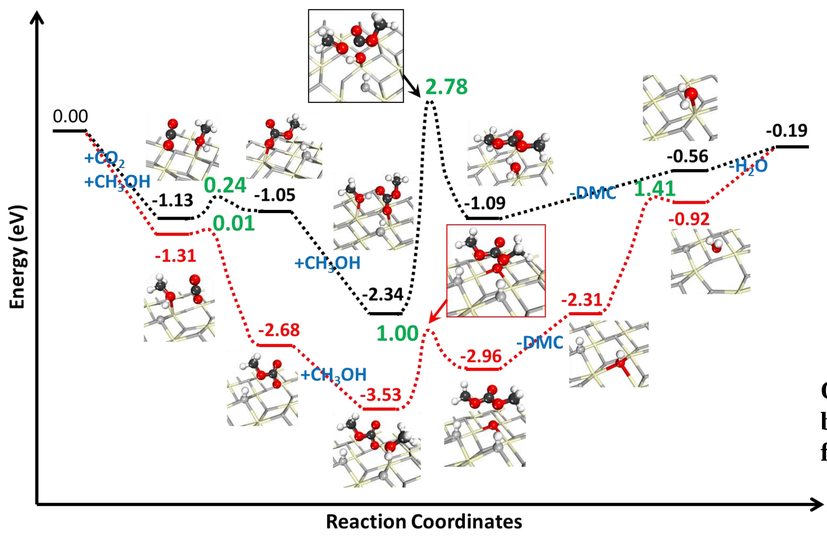
CO_2 AND METHANOL ADSORPTION

- Methanol and CO_2 show competitive adsorption energies on the oxygen vacancy site
- For CO_2, the bent adsorption is much more favorable but forms the unreactive carbonate species.



The dashed read circle: oxygen vacancy

FORMATION MECHANISM OF DMC: CI-NEB RESULTS



Black line:
pristine CeO_2 (p-CeO_2) surface

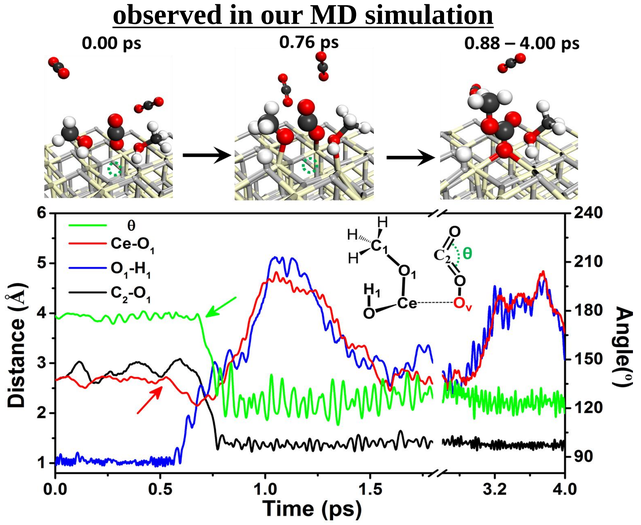
Red line:
CeO_2 surface with one oxygen vacancy (O_v-CeO_2)

Green number:
Activation barriers

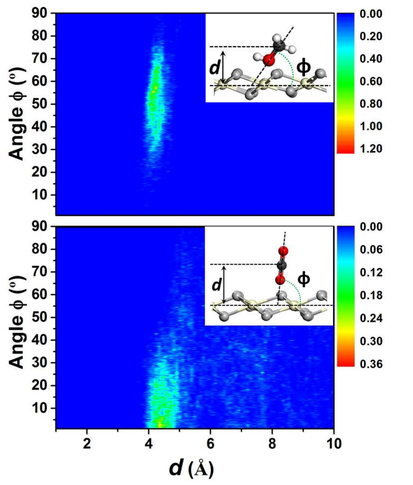
Oxygen vacancy lowers the barriers but hinders the formation of water molecules

MOLECULAR DYNAMICS SIMULATION

The formation of the key intermediate is observed in our MD simulation



Low population of vertical CO_2



SUMMARY OF MAIN FINDINGS

The formation mechanism of DMC:

Our CI-NEB results show that the formation of DMC on both p-CeO_2 and O_v-CeO_2 surfaces follows a similar Langmuir-Hinshelwood mechanism with both CO_2 and methanol adsorbing on the surface

The formation of the key intermediate (methyl carbonate) is directly observed in our molecular dynamics simulation, consistent with the extremely low barrier (0.01 eV) calculated by the CI-NEB method.

The promoting role of oxygen vacancy:

Based on the CI-NEB results, the existence of the oxygen vacancy can effectively lower the reaction barrier (2.78 eV → 1.00 eV) but hinders the removal of the water molecules.

One critical origin of the low rate of DMC:

The formation of the key intermediate with extremely low barrier requires the vertical adsorption of the CO_2 molecules. Unfortunately, the vertical adsorption of CO_2 is extremely unfavorable. Instead, CO_2 prefers to keep parallel to the CeO_2 surfaces.

In another word, the low population of the vertical adsorption of CO_2 is one major reason for the low rate of DMC.

REFERENCE

1. Marin, C. M.; Li, L.; Bhalkikar, A.; Doyle, J. E.; Zeng, X. C.; Cheung, C. L. Kinetic and Mechanistic Investigation of the Direct Synthesis of Dimethyl Carbonate from Carbon Dioxide over Ceria Nanorod Catalysts, **2016**, submitted.
2. Li, L; Zeng, X. C., Direct Simulation Evidence of Generation of Oxygen Vacancies at the Golden Cage Au_{16} and TiO_2 (110) interface. *J. Am. Chem. Soc.*, **2014**, *136*, 15857
3. Li, L.; Gao, Y.; Li, H.; Zhao, Y.; Pei, Y.; Chen, Z.; Zeng, X. C. CO Oxidation on TiO_2(110) Supported Subnanometer Gold Clusters: Size and Shape Effects. *J. Am. Chem. Soc.*, **2013**, *135*, 19336.
4. Honda, M.; Tamura, M.; Nakagawa, Y.; Sonehara, K.; Suzuki, K.; Fujimoto, K.; Tomishige, K. Ceria-catalyzed conversion of carbon dioxide into dimethyl carbonate with 2-cyanopyridine, ChemSusChem, **2013**, *6*, 1341.

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