The possible active sites and mechanism for methane oxidation over Pd/CeO$_2$ surface

Background

Methane is a clean, low-carbon and high-efficiency energy source and is abundantly found in natural gas, coal bed gas, shale gas and CH$_4$ clathrates. Methane is also a greenhouse gas with an effect that is 20 times higher than that of CO$_2$ (science, 337(2012)713-717). The relative abundance of CH$_4$ makes it an attractive alternative to methanol or oil. Moreover, the partial oxidation of methane to syngas (CO + H$_2$), has also become a potential process for the development of liquefied alcohols, synthetic fuels and light alkenes. In these processes, the methane activation is a key step on the catalysts.

Project and objective

The methane activation was mainly studied on the Pd-group metals, including the metal oxides. However, there are just a few papers examining the catalytic activity for methane oxidation over Pd/CeO$_2$ surface whether experiments or computations. Ceria is a good oxygen storage material, and palladium is a high hydrogen storage metal. If the methane is adsorbed on the interface between Pd metal and CeO$_2$ support, there are two pathways for metane activation. One is Pd metal attracts the hydrogen atom and methyl radical is captured by ceria lattice oxygens. One is converse.

Figure 1. The methane activation to form methyl group and hydrogen binding on lattice oxygen over single Pd/CeO$_2$(111) surface.

As mentioned in Fig. 1, the methane activation is facile. Then, the methyl radical can C-C couple to ethane (further couple and produce the long alkane, fuel) or be combusted to convert into CO$_2$ and H$_2$O in the rich of oxygen molecules. In this project, I mainly study the metane oxidation mechanism and examine the suitable catalyst model based on the CH$_4$ behavior simulation over Pd/CeO$_2$ interface. After considering the Van der Waal's correction (VDW), the methane can have a weak adsorption (adsorption energy is -0.23 eV over single Pd/CeO$_2$(111) surface).

Methodology

The VASP program software is employed to mimic the CH$_4$/O$_2$ behavior over various Pd/CeO$_2$ surfaces. With the PW-DFT method, the PBE functional is used (cutoff energy is 400 eV), as well as U (U=4.5 eV) correction due to the complicated computational treatment for 4f electrons of cerium atom. Moreover, the Van der Waal’s correction is also considered due to the weak adsorption of CH$_4$ on Pd/CeO$_2$ surface. For transition state search, the climbing NEB method is used.

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