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反応経路自動探索法を用いた表面光触媒反応の反応機構に関する研究

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[Background]

Heterogeneous photocatalytic oxidation of the organic compounds on semiconductor surface is an essential subject for studying the photocatalysis process.[1] In this work, we use phenol adsorbed on the anatase TiO_2(001) surface as the target model to examine the formation of excited state and the oxidation process after the excited state formation. A direct charge transfer excitation mechanism has been proposed in a previous study, resulting in a cationic state of phenol adsorbed on the anatase surface.[2] Based on this mechanism, we aim to figure out the how oxygen reacts with this cationic state to until the formation of final products.

[Method]

We use the plane wave DFT based code VASP to optimize the structure of phenol on anatase surface. The anatase surface is modeled as a 3 × 3 surface with a relatively large surface area (11.48 Å × 11.48 Å × 40 Å) for phenol adsorption. The AFIR method[3] implemented in the GRRM program is then used for an automated reaction pathway searching.

[Result]

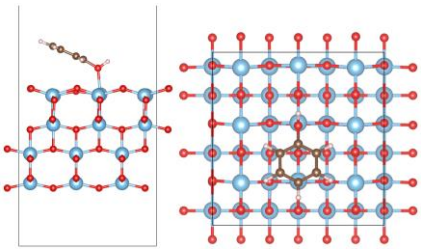

Fig. 1. side and top views of phenol on anatase surface

i). phenol adsorbed on anatase surface in ground state with a tilt angle as shown in **Fig. 1** is consistent with the previous study in which the Ti_6O_{12} cluster has been used;
ii). comparison between the calculated reaction pathways for reaction of phenol and O_2 molecule without the attendance of surface when phenol molecules are in their neutral and cationic states reveals that only the cationic state of phenol is reactive with O_2 molecule. 13 reactive IRCs in total have been predicted after the pathway searching;
iii). reaction route searching using the cationic phenol and O_2 as reactant predicts a bridge-like intermediate followed by a largely exothermic process to produce another stable intermediate. The surface effect will be introduced during the presentation day.

[Reference]

1. Photocatalysis: Fundamentals and Perspectives; Schneider, J., Bahnemann, D., Ye, J., Puma, G. L., Dionysiou, D. D., Eds.; Royal Society of Chemistry: Cambridge, 2016.
2. S. Suzuki, T. Tsuneda, and K. Hirao, *J. Chem. Phys*. **136**, 024706 (2012)
3. S. Maeda, et al., J. Comput. Chem., 39, 233 (2018)