Statusbericht

Studying selectivity and activity of NO_2 and water reactions on TiO_2 surface

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1 Current process and summary

To date, we have investigated the divergent behaviors of NO_2 and H_2O reaction on TiO_2 under dark condition and photo condition. In this work, we have employed an improved scheme to study the mechanisms of photoassisted $deNO_2$ reactions on the active sites of the anatase TiO_2(101) surface. The electronic structures and energies were calculated by using a GGA + LZ functional, which significantly improved the accuracy (comparable to calculations with the hybrid HSE06 functional) while maintaining the efficiency of normal GGA calculations. In addition, a novel algorithm was applied to study all possible reaction pathways and to obtain a global optimization of the limiting energies. It was found that the activity on the perfect surface is higher than on a defective one, because the strong OH* adsorption inhibits its combination with NO_2. We found the photogenerated hole to be more important for the perfect surface in tuning the reactivity. Because the hole is trapped by a reduced Ti on the defective surface, it has no effect on the adsorption energy of OH* species on the oxygen vacancy. In contrast, the OH* adsorption energy on a perfect surface can be weakened in the presence of the photogenerated hole, resulting in enhanced OH* conversion. We have proved the concept that the tunable reactivity in a charge-assisted process and diverse reaction pathways in photocatalysis are two methods that break the conventional scaling relation and the activity volcano plot limit under dark conditions, which is a quite critical insight for the design of photocatalysts.

Based on the the obtained results, we wrote and published the paper about $deNO_2$ on anatase TiO_2(101) surface on JPCL.

2 Publications

Pu Guo, Xiaoyan Fu, Peter Deák, Thomas Frauenheim, and Jianping Xiao. Activity and-Mechanism Mapping of Photocatalytic NO_2 Conversion on the Anatase TiO_2 (101)Surface.The Journal of Physical Chemistry Letters, 12(32):7708–7716, aug 2022