The tunable catalytic performance of supported single Pt atom on the graphene in propane direct dehydrogenation by rational doping

XiaoYing Sun, [a] Zhen Zhao[a, b*]

[a]*Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, China*

[b]*State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing,102249, China*

**Corresponding author: sunxiaoying78@163.com*

Abstract: The catalytic performance and reaction pathways of PDH on the supported single Pt atom are revealed from the first principle calculations with the emphasis on the tunable effects from doping of graphene support. The calculation indicates that the supported single Pt is an effective catalyst for propane activation with the largest barrier of 0.37 eV, which is comparable with the other Pt catalysts. Furthermore, the different support doping strategy can effectively modify the electronic structure of supported Pt atom. The nitrogen and boron dopings have the opposite effect on the charged state of Pt atom, which leads to the shift of the d-band center. The dissociation energy and reaction barrier of the first C−H bond breaking in propane has a strong dependence on the d-band center of supported Pt atom. It is therefore suggested that support doping is an effective method to tune the electronic structure of supported metal catalysts and consequently influence the catalytic performance.

Keywords: doping, single atom, dehydrogenation, support optimization

1. Introduction

The direct dehydrogenation of propane (PDH) is one of the most important industrial reactions to produce propylene. The platinum and chromium oxide are the conventional catalysts used in PDH. Especially, Pt is the industrial catalyst in Oleflex process of UOP company. The current biggest challenge of Pt catalysts in PDH is the deactivation caused by coking and side reactions. The coke formation is inevitable in PDH which will gradually cover the active sites and deactivate the catalysts. Generally, the Pt catalysts are periodically regenerated to remove coke. Many efforts are devoted to enhance the Pt's ability to resist the coke formation. Pt particle size, promoter, and catalyst support etc. are all proposed to have a major impact on the coke formation. In current work, the first principle calculations are performed on the supported single Pt atom on the nitrogen and boron-doped graphene. There are two major goals from the current study. Firstly, we want to examine the catalytic performance of the single Pt atom on the graphene support in PDH. Secondly, the support has a major effect on the performance of Pt catalyst in PDH. We intend to understand the working principle for the rational doping to maximize the catalytic performance.

2. Computational Setup

The calculations are performed by using periodic, spin-polarized DFT as implemented in Vienna ab initio program package (VASP). The electron-ion interactions are described by the projector augmented wave (PAW) method.

3. Results and discussion

There are several different configurations of the dopants on the graphene. Three nitrogens in pyridine group are distributed around a mono carbon vacancy. By using this configuration as the starting point, a serial dopant configuration on the graphene are built as the support for the single Pt atom as shown in figure 1. Not only the pure nitrogen or boron doping is considered, but also the dual dopants of nitrogen and boron are included. the charge of Pt atom generally has a trend from the positive charge state to the negative charge state from nitrogen doping, codoping to boron doping. The Pt on 3NG and 2NG support has the most positive charges, while the Pt on 3BG support has the most negative charges. The dissociation energy (E_{disso}) and the barrier (E_a) of the first C−H bond breaking are good indicators to evaluate the catalytic performance of the single Pt atom on the various supports as the first one is used to describe thermodynamics and the second one is used to calibrate kinetics. The single Pt atom on the graphene with high nitrogen dopants has more exothermic dissociation energy and lower reaction barrier. Furthermore, we found that there is a linear relation between dissociation energy, reaction barrier and the charges on Pt atom. It is suggested that positive charged Pt atom is more active for breaking C−H bond, and the Pt atoms on the 3BG and 3NG supports have the lowest and highest activity, respectively, for C−H bond activation by considering both dissociation energy and reaction barrier. The electronic structure of the supported Pt is continuously tuned by doping, which consequently modify the catalytic capabilities to break the C−H bond. Moreover, the dissociation energy and the activation barrier also have a linear relation which suggests that BEP is applicable to the single supported Pt atom catalysis. To further verify the reactivity of supported Pt on 3NG, the rate constant of the rate limiting step is calculated for PDH on single Pt at three different supports which are 3NG, vacG, and BG, respectively. In the related temperature range (600-800K), the rate constant on 3NG is at least one magnitude larger than the others. Side reaction pathway on Pt/3NG catalysts was also considered which starts from the primary hydrogen abstraction and leads to the formation of CH_3CH_2C. The second hydrogen abstraction barrier is 0.79 eV which is much bigger than the one on the pathway leading to the ethylene formation. Therefore the support single Pt also has good selectivity.

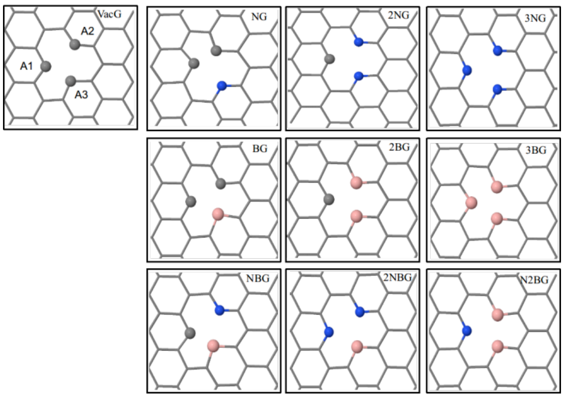

Figure 1. The configurations of the doped graphene support considered in current work. The dopants, nitrogen and boron, are varied around a mono-vacancy on graphene. The xNyBG notation indicates the number of nitrogen (x) and boron (y) on the doped graphene.3NG represents three nitrogens occupy the vacancy site and 2NBG represents two nitrogens and one boron (1 is omitted in this case). The undoped graphene with a mono vacancy is labeled as VacG.

4. Conclusions

The catalytic reaction pathways and performance of supported single Pt atom on the nitrogen and boron-doped graphene in the direct dehydrogenation of propane (PDH) are investigated by using first principle calculations. The different dopants on graphene have distinct effects on the electronic structure of the supported Pt atom. Consequently, the d-band center of Pt atom is modified by either nitrogen or boron doping. The nitrogen doping shifts the d-band center of Pt atom closer to the Fermi level compared with the boron doping and the pristine ones. On the other hand, the d-band center has a significant influence on the C−H bond dissociation energy and reaction barrier. Therefore, better reactivity of Pt is found on the support with more nitrogen dopants as the d-band center is closer to Fermi level. Also the calculated dissociation energy and the first C−H bond activation barrier obey the BEP rule. Among various investigated supports, the graphene doped by pyridine nitrogen is predicted to be the most effective for enhancing Pt catalytic performance. The current work shows the promising catalytic performance of supported single Pt atom in PDH. More importantly, the tunable properties of the supported metal catalysts on the carbon materials are achieved by the rational doping which provides a practical strategy for the catalyst optimization.