The active site, doping effect and reaction pathway of the dehydrogenation of hydrocarbons on the nanostructured carbon catalyst

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Abstract: A detailed description of the C2-C4 short alkane dehydrogenation are supplied from the first principles simulation. The focus is put on the active site identification, the doping effect (nitrogen and boron), and the rate estimation from kMC calculation. Not only conventional oxygen site but also carbon site on the catalysts is determined to be effective for C-H bond activation. BEP principle is found to be valid for dopants. The lateral interactions between adsorbates have a significant influence on the rate calculations. Moreover ODH on the carbon catalysts is suggested to follow a Mars-Krevelen mechanism.

Keywords: doping, carbon catalysts, dehydrogenation, kMC

1. Introduction

The nanostructured carbon catalysts such as carbon nanotube and graphene have been achieved tremendous developments in recent years[1]. The similar or even superior catalytic performance from the nanostructured carbon catalysts are found in various important chemical reactions such as oxidative dehydrogenation (ODH), oxygen reduction reaction, and selective oxidation in liquid phase compared with the conventional metal or metal oxide catalysts. In particularly, the ODH of hydrocarbons is one of the most successful applications of the nanostructured carbon catalysts. For example, the surface modified carbon nanotube catalyst applied in ODH of butane gives a two-times selectivity of butadiene than the best contemporary metal oxide catalyst[2]. Furthermore, the ODH of ethane, propane, butane and ethylbenzene all have been extensively investigated by using the nanostructured carbon catalysts. The further improvements of the carbon catalysts in ODH rely on the accurate description of the active site and reaction mechanism which can provide the optimization strategy. In current work, we are aiming to identify the active site, doping effect and reaction pathway of ODH of on the carbon catalysts by using first principles calculations.

2. Computational Setup

The most 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. The Fukui function calculations are done based on the cluster model by using NWChem.

3. Results and discussion

The Fukui function calculations are carried to understand the nucleophilicity of the oxygen functional groups at both armchair and zigzag edges[3,4]. As shown in Figure 1a, the calculations reveal that the diketone and quinone groups are the most nucleophilic ones among the investigated groups which indicate their potential to be the active site as the electrophilic groups will favor the combustion in ODH. The results also serve to judge the reactivity of the oxygen functional groups in other chemical reactions. Furthermore, the quinone and diketone groups are more reactive than the others by examining the dissociation energy of the ethane molecule. Therefore, the reaction path of ODH of ethane is explored at the diketone site and the results are shown in Figure 1b[5]. The barrier of the first C-H breaking is the largest one along the reaction path which implies it is the rate-limit step. On the other hand, the reaction intermediate, ethoxide, is very stable and detrimental to the selectivity. The calculations suggest that the radical pathway (RR in Figure 1b) is likely to be the favorable reaction process of the ODH reaction. The active sites evolve into the phenol groups after reaction and the regeneration of the active site is required to fulfill a catalytic cycle. The calculations uncover that the phenol groups are oxidized into H_2O_2 by the oxygen molecule to regenerate the diketone groups. It is noted that the mechanism of the regeneration is different from the metal oxide catalysts in ODH which has a formation of water to recover the active sites. Not only the quinone or diketone but also the ketone group which has only one C=O can also activate the C-H bond in propane. In previous studies, it is a pre-requisite that two neighboring carbonyl groups are needed for ODH reaction on the carbon catalyst as each of them abstracts a hydrogen atom. However the DFT calculations reveal that the single ketone group has the similar barrier and dissociation energy compared with quinone and diketone for the propane activation as shown in Figure 1c[6-9]. The carbon atom, which is bonded with oxygen in ketone group, participates into the C-H bond activation together with the oxygen. The Bade charge analysis reveals that the most charges go to the carbon rather than oxygen in ketone group during the propane activation. The complete catalytic cycle from the calculations verifies the possibility of ODH at the single ketone site. Furthermore, the rate and TOF of ODH of ethane is calculated under the reaction condition by microkinetic modeling as shown in Figure 1d.

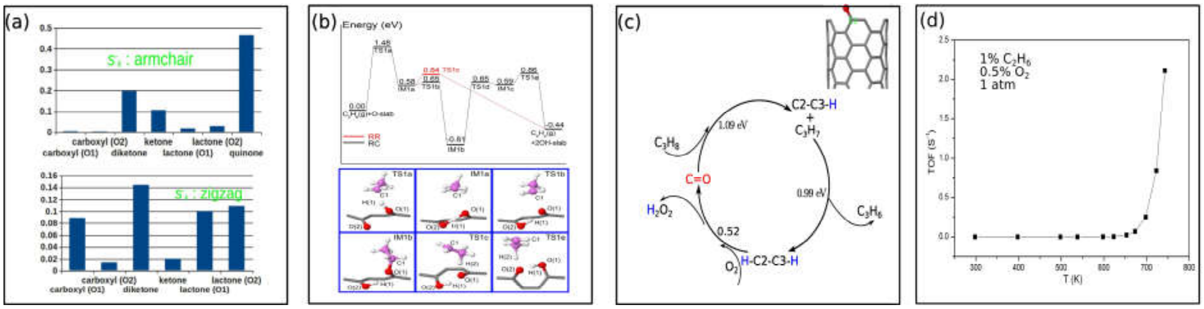

Figure 1. (a) The nucleophilicity of the oxygen functional groups from Fukui function calculations. (b) The reaction pathway and the important structures of ODH of ethane at diketone site. (c) The complete catalytic cycle of ODH at the single ketone site. (d) TOF of ODH of ethane from the DFT calculations.

4. Conclusions

The understandings of the active site and reaction pathway at the molecular level have a pivotal importance in catalysis. In current work, both diketone and single ketone groups are predicted to be the active site in ODH reaction. The most favorable reaction pathway is indicated and the complete catalytic cycle is presented for each of the active site. In particularly, the mechanism of the regeneration of active site is also included. Moreover the nucleophilicity of the oxygen functional groups are quantitatively evaluated for the first time which also serves as the reactivity descriptor. The reaction rate is obtained from the calculations by adopting the experimental condition. The results from the current work elucidate the catalytic property of the active site and the reaction process and pave the way to the further developments of the nanostructured carbon catalysts.

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