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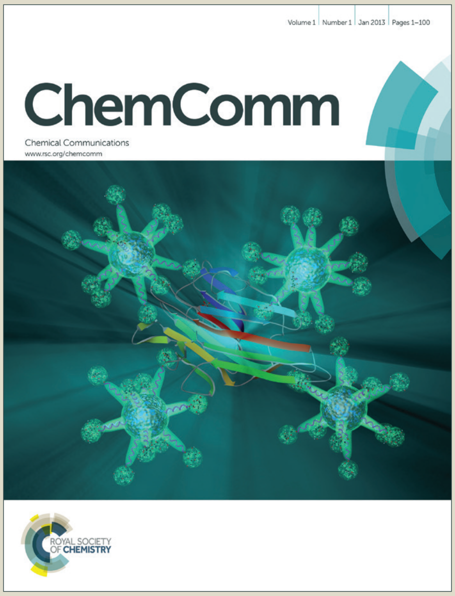

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Revealing the nature of the active site on the carbon catalyst for the C−H bond activation[†]

XiaoYing Sun,[a] Bo Li,[a] and Dangsheng Su*[a]

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A reactivity descriptor for the C−H bond activation on the nanostructured carbon catalyst is proposed. Furthermore the calculations reveal that the single ketone group can be an active site in ODH reaction.

In 2008, the researchers discovered that the surface modified carbon nanotube (CNT) catalyst can give a two-times bigger selectivity on the butadiene than the conventional V/MgO catalyst at the same conversion for the oxidative dehydrogenation (ODH) of butane.[1–4] This study is a kind of breakthrough for the ODH reaction. Not only the catalyst is a metal-free carbon based material which is environmentally and economically attractive[5–8] but also the much improved yields of the desired alkene could be beneficial for the ODH reaction toward the industrial applications. The oxygen species is the key element which renders the catalytic ability of the carbon catalyst in the ODH reaction. It has been shown the catalytic performance is greatly improved after the oxidizing treatment in the ODH reaction.[1,9] Furthermore, the most studies indicate that the ketonic-like groups such as ketone and quinone are the active centers during the reaction.[1,10–13] Interestingly, this conclusion is valid for the various carbon catalysts such as CNT, nanodiamond, nanofiber, and activated carbon although they have very different structures.

Although the importance of the oxygen species is well established and the active sites assignment is seemingly to unambiguously reach an agreement, there are still a few open questions remaining which are worth for the further explorations. First of all, it is still a challenge to evaluate the reactivity of the different oxygen functional groups at the same footing. This issue is naturally aroused as the reactivity of the oxygen functional groups varies under the different chemical environments. For example, the same oxygen functional group at the different edges of the carbon nanotube is expected to have the different capabilities towards the C−H bond activation. In current work, a descriptor is proposed and tested for the reactivities of the various oxygen functional groups. Moreover, the spotlight is exclusively on the oxygen functional groups on the nanostructured carbon catalysts in literature for the C−H bond activation in ODH. It is an intriguing question that there are any other factors will also play a role.

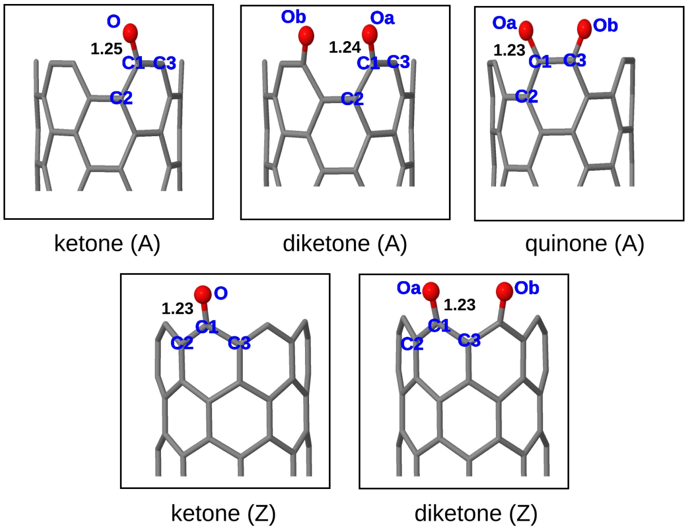

Fig. 1 The optimized structures of the oxygen functional groups on (5,5) SWCNT and (8,0) SWCNT. The bond distance (black, Å) between the oxygen and carbon (C1) is listed. The A or Z in bracket indicates the armchair (5,5) or zigzag (8,0) SWCNTs respectively. Color code: carbon is gray and oxygen is red. The hydrogens saturating the edges are not shown.

To achieve the above mentioned objectives, the activation of propane on the single-walled carbon nanotube (SWCNT) is selected as a model reaction to explore the nature of the active site on the carbon catalyst for the C−H bond activation. The ketone and quinone groups on both (5,5) and (8,0) SWCNT are chosen to represent the oxygen functional groups. In addition, the carbon atom which is bonded with the oxygen is also considered in the calculations as a candidate for the active site besides the oxygen functional group. We carried out the detailed studies on the primary C−H bond breaking at the

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[a]Address: Shenyang National Laboratory for Materials Science , Institute of Metal Research, Chinese Academy of Sciences 72 Wenhua Road, Shenyang 110016, China. E-mail: dssu@imr.ac.cn

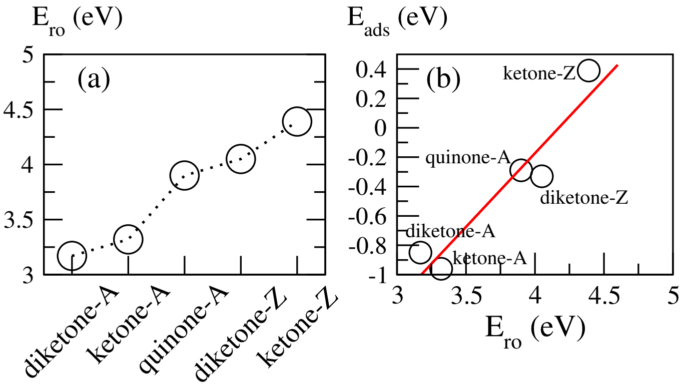

Fig. 2 (a) The calculated E_{ro} of the various oxygen functional groups. (b) The relationship between E_{ro} and the adsorption energy (E_{ads}) of the hydrogen atom.

various active sites as it is probably the rate-limiting step in the ODH reaction.[14] The dissociation energies and the barriers at the various sites are calculated and compared. The second hydrogen abstraction and the re-oxidation of the catalyst are also investigated for a complete catalytic cycle. Using the electronic structure analysis, the deeper understandings on the nature of the active center are achieved. The current work further advances the understandings on the properties of the nanostructured carbon catalysts and indicates possible applications in future.

The optimized structures of ketone, diketone, and quinone groups at both (5,5) SWCNT and (8,0) SWCNT are shown in Fig. 1. The bond distance between the oxygen and the carbon is from 1.23 to 1.25 Å. The calculated bond distance is close to the C=O bond distance (1.22 Å) and nearly 0.2 Å shorter than the C−O bond distance (1.43 Å).[15] It indicates that the C=O bonds are formed for the investigated oxygen functional groups. Furthermore, the Bader charge analysis[16] is carried out for the oxygen functional groups and listed in Table S1. Considering the difference in the electronegativity of the carbon and oxygen, it is not surprise to observe that the electrons are transfered from the carbon to the oxygen, which leads to the positively and negatively charged carbon and oxygen respectively. This charge transfer is found to be restricted within the oxygen and its bonded carbon atom (C1 in Fig. 1). The charges of the other carbons around the oxygen have no any significant variations. After the charge transfer, the oxygen obtains around 1 *e* while carbon (C1 in Fig. 1) which is bonded to oxygen loses that amount of electrons. So far, the oxygens in the different functional groups at both (5,5) and (8,0) SWCNTs have the similar behavior regarding of the bond distance and the obtained charges. However they show some different features in the partial density of states (PDOS) of the oxygen as shown in Fig. S1. From the PDOS, the ketone (A) and diketone (A) groups have states around the Fermi level. For the others, the highest occupied states from the oxygen are not adjacent to the Fermi level. This implies that the oxygens in the different functional groups might have the different reactivities.

To evaluate the reactivity of the oxygen functional groups, the energy (E_{ro}), which is required to remove oxygen atom from SWCNT, is calculated and compared. The E_{ro} of the different oxygen functional groups are shown in Fig. 2a. From Fig. 2a, the E_{ro} of the diketone (A), ketone (A), quinone (A), diketone (Z), and ketone (Z) is in a increasing order. This indicates that the oxygens in the diketone (A) are probably the most reactive, while the one in the ketone (Z) is the least reactive. The sequence in E_{ro} is consistent with the position of the highest occupied states of the oxygen relative to the Fermi level as shown in Fig. S1. The states from the diketone (A) and ketone (A) are the most close to the Fermi level and they have the smallest E_{ro}. To corroborate the judgement on the reactivities of the oxygen, the hydrogen atom adsorptions are calculated at the different oxygen functional groups. In Fig. 2b, the calculated adsorption energies are in a good linear relationship with the calculated E_{ro}. The oxygen functional group with the smaller E_{ro} yields the more exothermic adsorption energies. To some extent, this suggests that the E_{ro} is an useful reactivity descriptor for the oxygen functional groups on the carbon catalysts.

For carbon catalyst, the oxygen functional group is the most important factor as the oxidation treatment is indispensable for the observed catalytic performance in ODH. The introduction of oxygens to the carbon catalysts is not only leading to the formation of various functional groups but also brought changes to the carbon, which is the anchoring site for the oxygen. The change of the carbon is clearly manifested in Table S1. Upon the bonding to oxygen, the carbon (C1 in Fig. 1) loses electrons and become positively charged. It is reasonable to expect the reactivities of the carbon are modified after interacting with the oxygen. To further clarify this issue, the dissociation energy (E_d) and the barrier (E_a) for the primary C−H bond breaking in propane are calculated. For the propane dissociative adsorption, there are generally two sites available for the C_3H_7 and H to bind which are usually oxygens on the carbon catalyst. For the ketone (A) which has only one oxygen, there is a need for another site to be available for the dissociation to proceed. From Table 1, it is indicated the C1 in Fig. 1 can be an active center in the propane dissociation. The E_d and E_a at the O-C1 site for the propane dissociation is 0.49 and 1.09 eV respectively. From the calculations, it is possible that the carbon atom participates in the propane activation on the carbon catalyst together with the oxygen.

For the quinone and diketone groups, they have two oxygens in each functional group. For the propane dissociation at these groups, the active sites can be either oxygen-oxygen

Table 1 The dissociation energy (E_d, eV) and barrier (E_a, eV) of the primary hydrogen abstraction in propane at the different oxygen functional groups. The dissociation sites are indicated in Fig. 1. The O-C1 means the sites for the dissociated H and C_3H_7 to bind respectively. The negative E_d means exothermic.

groups	dissociation site	E_d	E_a
ketone (A)	O-C1	0.49	1.09
diketone (Z)	Oa-Ob	0.74	1.44
	Oa-C1	-0.40	1.78
diketone (A)	Oa-Ob	-1.25	1.56
	Oa-C1	-0.29	1.49
quinone (A)	Oa-Ob	0.04	1.21
	Oa-C1	-0.41	1.86

Table 2 The charge variations during the propane dissociation on the (5,5) SWCNT. The labelled atoms are shown in Fig. S3.

H1	O3	C5	C7
0.64	-0.20	-0.49	0.02
C2	O4	C6	C8
0.47	-0.02	-0.40	0.02

or oxygen-carbon combinations for the H and C_3H_7 to bind. It is interesting to see that the E_d is more exothermic for the oxygen-carbon (Oa, C1) site than the oxygen-oxygen site (Oa, Ob) for the diketone (Z) and quinone (A) groups as shown in Table 1. This indicates that the carbon (C1) is thermodynamics more reactive than the oxygen which is not expected in the first place. In addition, the barrier of the dissociation is comparable for oxygen-oxygen and oxygen-carbon sites which are 1.44, 1.21 and 1.78, 1.86 eV respectively. The similar observations are also found for the dissociation at the diketone (A). Although the E_d is more endothermic at the oxygen-carbon (Oa, C1), the barrier is still close to each other between oxygen-oxygen (Oa, Ob) and the oxygen-carbon (Oa, C1) sites. The optimized structures of the dissociated propane at the diketone group are shown in Fig. S2 which reveals that the C_3H_7 and H binds either at the O-O site or the O-C site respectively. The comparable performance for the activation of C−H bond at the diketone (Z) and quinone groups is also discussed in the previous theoretical calculations.[17] The calculations demonstrate that the carbon does has the ability for the C−H bond activation in propane and is comparable with the oxygen reactivity in some cases. In fact, the reactivity of the positive carbon atom, which is abbreviated as carbocation, has already been interpreted in the organic chemistry textbook.[15] It has been suggested that the carbocation is a good electron acceptor to interact with the nucleophiles.

In order to further understand the properties of carbocation, the charge transfer during the C−H bond breaking is analyzed on the (5,5) SWCNT. From Table 2, it is clearly indicated that the charges of the propane dissociated fragments, C_3H_7 and H (C2 and H1 in Fig. S3), are decreased and they become positively charged. The majority of the charges go to the carbons (C5 and C6 in Fig. S3) instead of the oxygens. The observations prove that the carbocations formed after bonding with oxygen are good electron acceptors. The analysis once again reveals that the carbon is not a spectator in the C−H bond activation and has been actively participated during the activation.

Furthermore, the second hydrogen abstraction at the ketone (A) group and the re-oxidation of catalyst are investigated to fulfill a catalytic cycle. As shown in the Fig. 3a, the adsorbed alkyl surmounts a barrier of 1.56 eV to lose the second hydrogen and the desired product propylene is formed. The propylene can also obtained through a radical mechanism as shown in Fig. 3b. The C_3H_7 radical, which forms after the first C−H breaking, interacts with the carbon atom (C1 in Fig. 1) to form the propylene and the calculated barrier is 0.97 eV. Regardless of which path to proceed, the ketone group evolves into the -OH and -CH after the propylene formation. To regenerate the active sites, the oxygen molecule is introduced as the oxidant. As shown in Fig. S4, the oxygen molecule captures the two hydrogens and becomes a H_2O_2. The active sites (O1 and C1 in ketone group) are thus recovered and the barrier of the process is 1.47 eV. The similar re-oxidation mechanism is also discussed in the other studies.[17,18] The calculations demonstrate that the single ketone group can serve as an active site in the ODH reaction which is not widely perceived in literature.

In conclusions, the nature of the active sites on carbon catalyst for the C−H bond activation is studied by the DFT calculations. The reactivities of several oxygen functional groups are examined and compared. A descriptor for the oxygen reactivity on the carbon catalyst is proposed which is the energy required for the oxygen removal. The calculations of the hydrogen adsorption give the credits for this proposed descriptor. It is very interesting to observe that the carbon atom can participate in the activation of propane molecule. The unexpected reactivity from the carbon is partly attributed as the formation of the carbocation. Moreover, the good electrophilic ability of the carbocation is clearly indicated in the charge transfer during the C−H bond breaking of propane. Furthermore the propylene formation and the re-oxidation of the catalysts are also explored at the ketone group. The results indicate the possibility that the O-C site can be complementary to the O-O site as the active center in the ODH reaction. Overall, the current study brings the new perspective on the nature of the active site on the carbon catalyst and the results from the current work are very meaningful in the

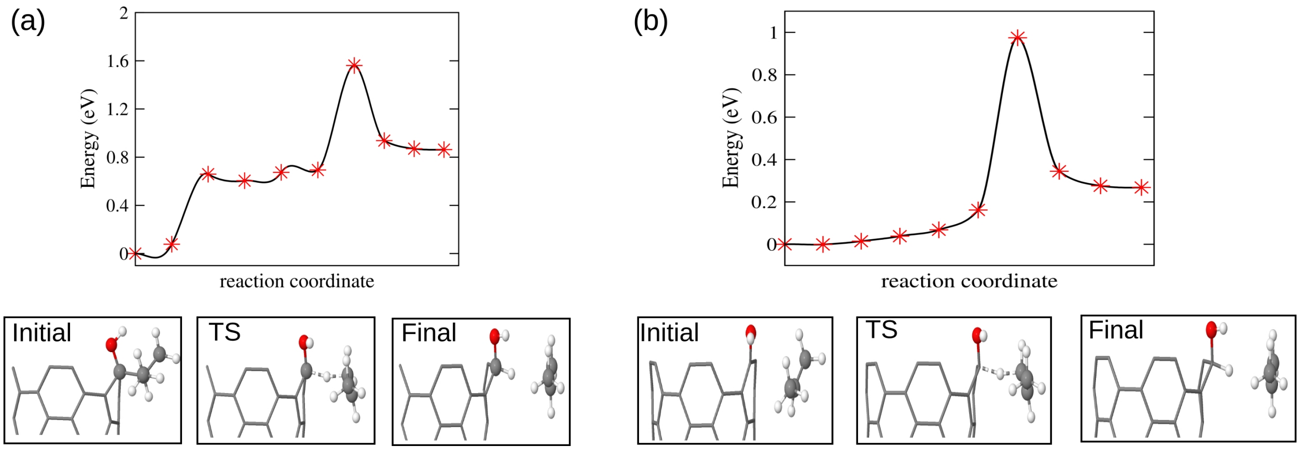

Fig. 3 The reaction path and the important structures on the reaction path (the initial state (Initial), the transition state (TS), and the final state (Final)) of the second hydrogen abstraction and the formation of the propylene at the ketone (A) group. (a) the hydrogen abstraction from the adsorbed C_3H_7 (b) the hydrogen abstraction from the C_3H_7 radical. Color code is same with Fig. 1.

interpretation of the related experimental observations.

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