Revealing the nature of the active site on the carbon catalyst for C–H bond activation†

XiaoYing Sun, Bo Li and Dangsheng Su*

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 show two-times higher selectivity for butadiene than the conventional V/MgO catalyst in 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 is the catalyst a metal-free carbon based material which is environmentally and economically attractive5–8 but also the much improved yields of the desired alkene could be beneficial for the ODH reaction toward 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 that the catalytic performance is greatly improved after the oxidation treatment in the ODH reaction.9,10 Furthermore, 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 CNTs, nanodiamonds, nanofibers, and activated carbon although they have very different structures.

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

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 C–H bond activation. The ketone and quinone groups on both (5,5) and (8,0) SWCNTs are chosen to represent the oxygen functional groups. In addition, the carbon atom which is bonded to the oxygen atom is also considered in the calculations as a candidate for the active site besides the oxygen functional group. We carried out detailed studies on the primary C–H bond breaking at the various active sites as it is probably the rate-limiting step of 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 understanding of the nature of the active center is achieved. The current work further advances the understanding of the properties of the nanostructured carbon catalysts and indicates their possible applications in the future.

The optimized structures of ketone, diketone, and quinone groups on both (5,5) SWCNTs and (8,0) SWCNTs 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 This indicates that the C–O bonds are formed for the investigated oxygen functional groups. Furthermore, the Bader charge analysis16 is carried out for the oxygen functional groups and listed in Table S1 (ESI†). Considering the difference in the electronegativity of the carbon and oxygen, it is not a surprise to observe that the electrons are transferred from the carbon to the oxygen, which leads to the positively and negatively charged carbon and oxygen...
can observe that the oxygen functional groups is shown in Fig. 2a. From Fig. 2a we
not adjacent to the Fermi level. This implies that the oxygen atoms
in the different functional groups might have different reactivities.

To evaluate the reactivity of the oxygen functional groups, the
element (E_{ro}), which is required to remove oxygen atoms from SWCNTs, is calculated and compared. The E_{ro} of the different oxygen functional groups is shown in Fig. 2a. From Fig. 2a we can observe that the E_{ro} of the diketone (A), ketone (A), quinone (A), diketone (Z), and ketone (Z) is in an increasing order. This indicates that the oxygen atoms in the diketone (A) are probably the most reactive, while the one in the ketone (Z) is the least reactive. The trend 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 (ESI†). The states of the diketone (A) and ketone (A) are closest to the Fermi level and they have the smallest E_{ro}. To corroborate the judgement on the reactivities of the oxygen, the hydrogen atom adsorption energies are calculated on 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 a useful reactivity descriptor for the oxygen functional groups on the carbon catalysts.

For carbon catalysts, 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 oxygen atoms into the carbon catalysts not only leads to the formation of various functional groups but also brings about changes in carbon, which is the anchoring site for oxygen. The change in the carbon is clearly manifested in Table S1 (ESI†). Upon bonding to oxygen, carbon (C1 in Fig. 1) loses electrons and becomes positively charged. It is reasonable to expect that the carbon atom participates in the propane activation on the carbon catalyst 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 1e while carbon (C1 in Fig. 1) which is bonded to oxygen loses that amount of electrons. So far, the oxygen atoms in the different functional groups in both (5,5) and (8,0) SWCNTs have a similar behavior regarding 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 (ESI†). From the PDOS, we can see that the ketone (A) and diketone (A) groups have states around the Fermi level. For the others, the highest occupied states of the oxygen are not adjacent to the Fermi level. This implies that the oxygen atoms in the different functional groups might have different reactivities.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Dissociation site</th>
<th>$E_d$ (eV)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketone (A)</td>
<td>O–C1</td>
<td>0.49</td>
<td>1.09</td>
</tr>
<tr>
<td>Diketone (Z)</td>
<td>Oa–Ob</td>
<td>0.74</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>Oa–C1</td>
<td>−0.40</td>
<td>1.78</td>
</tr>
<tr>
<td>Diketone (A)</td>
<td>Oa–Ob</td>
<td>−1.25</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>Oa–C1</td>
<td>−0.29</td>
<td>1.49</td>
</tr>
<tr>
<td>Quinone (A)</td>
<td>Oa–Ob</td>
<td>0.04</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>Oa–C1</td>
<td>−0.41</td>
<td>1.86</td>
</tr>
</tbody>
</table>

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. O–C1 means the sites for the dissociated H and C_3H_7 to bind respectively. Negative $E_a$ means exothermic.
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 thermodynamically more reactive than the oxygen which is not expected in the first place. In addition, the barrier of dissociation is comparable for oxygen–oxygen and oxygen–carbon sites which are 1.44, 1.21 and 1.78, 1.86 eV respectively. 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) site, the barrier is still close to each other between the oxygen–oxygen (Oa, Ob) and oxygen–carbon (Oa, C1) sites. The optimized structures of the dissociated propane at the diketone group are shown in Fig. S2 (ESI†) which reveal that C$_3$H$_7$ and H bind either at the O–O site or the O–C site respectively. The comparable performance for the activation of the C–H bond at the diketone (Z) and quinone groups is also discussed in the previous theoretical calculations. The calculations demonstrate that the carbon does have the ability for 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 known as a carbocation, has already been interpreted in the organic chemistry textbook. It has been suggested that a carbocation is a good electron acceptor to interact with the nucleophiles.

In order to further understand the properties of the carbocation, the charge transfer during C–H bond breaking is analyzed on the (5,5) SWCNT. Table 2 shows the charge variations of the propane dissociated fragments, C$_3$H$_7$ and H (C2 and H1 in Fig. S3, ESI†), are decreased and they become positively charged. The majority of the charges go to the carbon atoms (C5 and C6 in Fig. S3, ESI†) instead of the oxygen atoms. 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 actively participates during activation.

Furthermore, the second hydrogen abstraction at the ketone (A) group and the re-oxidation of the catalyst are investigated to complete a catalytic cycle. As shown in Fig. 3a, the adsorbed alkyl surmounts a barrier of 1.56 eV to lose the second hydrogen and the desired product propylene is formed. Propylene can also be obtained through a radical mechanism as shown in Fig. 3b. The C$_3$H$_7$ radical, which forms after the first C–H bond 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 –OH and –CH after propylene formation. To regenerate the active sites, the oxygen molecule is introduced as the oxidant. As shown in Fig. S4 (ESI†), the oxygen molecule captures the two hydrogen atoms and becomes H$_2$O$_2$. The active sites (O1 and C1 in the ketone group) are thus recovered and the barrier of the process is 1.47 eV. A similar re-oxidation mechanism is also discussed in the other studies. The calculations demonstrate that the single ketone group can serve as an active site in the ODH reaction which is not widely perceived in the literature.

In conclusion, the nature of the active sites on the 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 energy give the credits for this proposed descriptor. It is very interesting to observe that the carbon atom can participate in the activation of the propane molecule. The unexpected reactivity of the carbon is partly attributed to the formation of the carbocation. Moreover, the good electrophilic ability of the carbocation is clearly indicated in the charge

| Table 2 Charge variations during the propane dissociation on the (5,5) SWCNT. The labelled atoms are shown in Fig. S3 (ESI†) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | O1              | O3              | C5              | C7              |
| H1              | +0.64           | −0.20           | −0.49           | 0.02            |
| C2              | +0.47           | −0.02           | −0.40           | 0.02            |

(a) Hydrogen abstraction from the adsorbed C$_3$H$_7$ and (b) hydrogen abstraction from the C$_3$H$_7$ radical. Color code is the same as Fig. 1.
transfer during the C–H bond breaking of propane. Furthermore, propylene formation and 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 a new perspective on the nature of the active site on the carbon catalyst and the results of the current work are very meaningful for the interpretation of the related experimental observations.

This work is supported by MOST (2011CBA00504) and NSFC of China (21133010, 51221264, 21261160487), “Strategic Priority Research Program” of the Chinese Academy of Sciences, Grant No. XDA09030103. B.L. is supported by a SYNL-T.S. K Research Fellowship. B.L. thanks the financial grant from the Institute of Metal Research (Y3NBA211A1) and China Postdoctoral Science Foundation (2012M511186). The computing time is partly allocated from ShenYang Branch, Supercomputing Center of CAS.

References

13 B. Li and D. Su, Chem. – Asian J., 2013, 8, 2605–2608.