# Quantum-chemical investigation of hydrocarbon oxidative dehydrogenation over spin-active carbon catalyst clusters

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**Supplementary A**
*Modelling of hydrocarbons ODH (computational details)*

Methane demonstrates the simplest behaviour. Over all carbon clusters and in all multiplicity states it reacts under formation of a $CH_3^{\cdot}$ radical and a surface C–OH group.

The reaction pathways for higher hydrocarbons strongly depend on the multiplicity state of the carbon cluster. The reaction of ethane with the quinone groups of the **Z9GO$_5$** cluster produces a $C_2H_5^{\cdot}$ radical and a surface C–OH group only in quintet state, whereas in triplet and BS singlet the reaction results in a surface ether C–O$C_2H_5$ due to the instant reaction of the resulting $C_2H_5^{\cdot}$ radical with the neighbouring quinone groups. The same holds for the first stage activation of the methylene C–H bond in propane by the **Z9GO$_5$** cluster. However, the elimination of the methyl H atom from the propane molecule results in a $C_3H_7^{\cdot}$ radical even in

triplet state. In the case of the carbon cluster also the $E_a$ values of the reaction depend on the multiplicity state of the system and decrease with increasing multiplicity. On the other hand, within the same multiplicity state the $E_a$ value decreases in the order methane > ethane > propane (methylene C–H).

If the radical resulting from the first stage of ODH reacts with a neighboured quinone group on the same carbon cluster **Z9GO$_5$H** (now partially reduced) the $E_a$ values are higher than the reaction barriers of primary C–H activation. It suggests that the second stage is limiting the overall reaction, which is opposite to the trend over metal oxide catalysts [X. Rozanska, J. Sauer Int. J. Quant. Chem. 108, (2008) 2223]. Also if we consider a gas-phase transport of the radical to a different highly oxidized reaction site or meanwhile reoxidation of the cluster, the reaction of $C_2H_5^{\cdot}$ with the completely oxidized zigzag edge in sextet (i.e., with the carbon cluster in quintet state) has an activation energy comparable to the latter one. Here, in quartet state (i.e., with the carbon cluster in triplet state) again a surface ether is formed with almost the same $E_a$ and much more stable initial and final states.

Ethylbenzene reacts with the **Z9GO$_5$** cluster in completely different manner. A benzyl radical is produced in quintet, whereas two H atoms are eliminated under formation of styrene in one act in triplet state (one can note that a benzyl anion is formed as an intermediate in this case); in singlet state a C-O-CH($CH_3$)Ph benzyl surface ether is formed by subsequent addition of the reaction intermediate to a neighbouring quinone group. Here, activation energies are much lower (18.8–27.1 kJ mol$^{-1}$) than that of the light alkanes activation. However, in quintet state the $E_a$ value for the second H atom abstraction is 3 times higher than that for the first one, indicating a high stability of the benzylic radical.

The reactivity type of the **Z8GO$_4$** cluster in respect to $C_2H_6$ and ethylbenzene is opposite to **Z9GO**. All multiplicity states considered for the reaction with ethane demonstrated the ODH mechanism (with ethylene formed in one stage in triplet) with barriers comparable to that over the **Z9GO$_5$** cluster. Here, ethylbenzene is much less reactive and the reaction results in surface

ethers for multiplicity states other (lower) than $M_{max}$ and in a benzyl radical in $M_{max}$ (i.e., quintet). As it is the case for the **Z9GO$_5$** cluster the abstraction of the second H atom of ethylbenzene in methyl position is rate-limiting.

Therefore, the reactions of hydrocarbons with the quinone group saturated zigzag edge of different shapes of carbon clusters share some similar features. In $M_{max}$ state the first stage of the reaction always leads to hydrocarbon radicals. In lower multiplicity states the resulting mono-dehydrogenized species either attaches to a neighbouring quinone group forming a surface ether, or evolve as a RH$^{\cdot}$ radical. An effect of the shape of the zigzag edge carbon cluster on the outcome of the reaction might be explained ambiguously and requires additional studies.

A restricted Kohn-Sham (RKS) formalism was applied in one model reaction of ethane to **Z9GO5** cluster. In this approach no unpairing of electrons is allowed, so the mechanism of the reaction is restricted to acid/base type. The reaction results in formation of surface ether, as in the case of non-maximal stable spin states in UKS formalism. This is also consistent with data on propane ODH through heterolytic C–H bond dissociation that leads to attachment of the propyl radical to the catalyst backbone [X. Rozanska, R. Fortrie, J.Sauer, J. Phys. Chem. C 111, (2007) 6041]. Hence, the acid/base mechanism of light alkane reaction with the oxidized graphitic edge is analogous by product to the non-ODH process in radical-type mechanism.

The armchair-edge cluster **A8GO$_4$** is much less reactive in respect to neutral hydrocarbon molecules than the zigzag-terminated ones. Surface ethers are formed in the case of ethane and ethylbenzene ODH with activation energies equal to 147.9 and 127.7 kJ mol$^{-1}$, respectively. It suggests that the armchair edge can be considered as passive in comparison to the zigzag termination. However, the reaction barrier of the **A8GO$_4$** cluster to an ethyl radical is extremely low (~6 kJ mol$^{-1}$). Here, the formation of surface ether or ethylene depends on the initial orientation of the $C_2H_5^{\cdot}$ radical. Therefore, the quinone group terminated armchair edge can act as a reacting agent in respect to hydrocarbon radicals, which were previously formed on a zigzag

edge and, consequently, a transport stage between such areas with different type of edge termination might play a crucial role in the ODH overall process.

Table S1. Energy barriers $\Delta H_0^{\ddagger}$, $\Delta G_0^{\ddagger}$ in TS, and $\Delta_r G^0$ values of the reactions of hydrocarbons with **Z9GO$_5$** and **Z9GO$_5$H$_2$** clusters.

| Reacting species | *M* | TS distance / Å | $\Delta G_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta H_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta_r G_0$ / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| Z9GO$_5$ + CH$_4$ | BS 1 | 1.242 | 117.81 | 104.10 | 24.52 |
| | 3 | 1.220 | 119.93 | 97.96 | 23.89 |
| | 5 | 1.178 | 104.09 | 94.04 | 16.79 |
| Z9GO$_5$ + C$_2$H$_6$ | BS 1 | 1.224 | 93.43 | 82.88 | –184.31 |
| | 3 | 1.259 | 79.118 | 70.75 | –207.54 |
| | 5 | 1.195 | 64.63 | 59.74 | 10.20 |
| Z9GO$_5$H$^{\cdot}$ + C$_2$H$_5^{\cdot}$ | 5 | 1.250 | 91.78 | 88.88 | –30.26 |
| Z9GO$_5$ + C$_2$H$_5^{\cdot}$ | 6 | 1.242 | 98.76 | 99.18 | 11.50 |
| Z9GO$_5$ + C$_3$H$_8$ (1H)[a] | 3 | 1.266 | 82.75 | 79.68 | 2.90 |
| | 5 | 1.219 | 65.28 | 63.22 | –12.16 |
| Z9GO$_5$H$^{\cdot}$ + CH$_3$CH$_2$CH$_2^{\cdot}$ | 3 | 1.144 | 107.59 | 95.16 | –222.12 |
| | 5 | 1.262 | 91.86 | 75.03 | –33.87 |
| Z9GO$_5$ + C$_3$H$_8$ (2H)[b] | 3 | 1.302 | 73.86 | 74.55 | –147.81 |
| | 5 | 1.269 | 45.13 | 44.85 | –38.02 |
| Z9GO$_5$H$^{\cdot}$ + CH$_3$C$^{\cdot}$HCH$_3$ | 5 | 1.270 | 94.76 | 97.48 | 1.58 |
| Z9GO$_5$ + PhEt | BS 1 | 1.357 | 27.73 | 18.81 | –168.39 |
| | 3 | 1.415 | 20.70 | 25.15 | –301.07 |
| | 5 | 1.325 | 30.65 | 27.12 | –63.86 |
| Z9GO$_5$H$^{\cdot}$ + PhC$^{\cdot}$HCH$_3$ | 5 | 1.129 | 79.32 | 82.55 | 8.55 |
| Z9GO$_5$H$_2$ + PhEt | BS 1 | 1.333 | 26.05 | 35.62 | -64.66 |
| Z9GO$_5$H$_2$ + PhEt | 3 | 1.283 | 47.42 | 47.31 | -45.25 |

[a] Activation of methyl C-H bond
[b] Activation of methylene C-H bond

Table S2. Energy barriers $\Delta H_0^{\ddagger}$, $\Delta G_0^{\ddagger}$ in TS, and $\Delta_r G^0$ values of the reactions of hydrocarbons with **Z8GO$_4$** cluster.

| Reacting species | *M* | TS distance / Å | $\Delta G_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta H_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta_r G_0$ / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| Z8GO$_4$+ C$_2$H$_6$ | BS 1 | 1.260 | 107.75 | 108.86 | 22.46 |
| | 3 | 1.244 | 93.15 | 93.34 | –251.81 |
| | 5 | 1.219 | 96.97 | 91.08 | –7.64 |
| Z8GO$_4$H$^{\cdot}$ + C$_2$H$_5^{\cdot}$ | 5 | 1.236 | 126.30 | 106.84 | –15.22 |
| Z8GO$_4$+ C$_2$H$_5^{\cdot}$ | 6 | 1.248 | 109.33 | 103.48 | 7.59 |
| Z8GO$_4$+ PhEt | BS 1 | 1.304 | 65.76 | 58.59 | –140.25 |
| | 3 | 1.309 | 53.71 | 55.37 | –150.46 |
| | 5 | 1.260 | 54.94 | 54.36 | –40.98 |
| Z8GO$_4$H$^{\cdot}$ + PhC$^{\cdot}$HCH$_3$ | 5 | 1.124 | 95.36 | 99.00 | 5.33 |

Table S3. Energy barriers $\Delta H_0^{\ddagger}$, $\Delta G_0^{\ddagger}$ in TS, and $\Delta_r G^0$ values of the reactions of hydrocarbons with **A8GO$_4$** cluster.

| Reacting species | *M* | TS distance / Å | $\Delta G_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta H_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta_r G_0$ / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| A8GO$_4$ + C$_2$H$_6$ | BS 1 | 1.084 | 145.27 | 147.91 | 137.96 |
| A8GO$_4$ + C$_2$H$_5^{\cdot}$ | 2 | 1.472 | 4.83 | 5.75 | –118.61 |
| A8GO$_4$ + PhEt | BS 1 | 1.111 | 122.59 | 127.69 | 0.23 |

Table S4. Energy barriers $\Delta H_0^{\ddagger}$, $\Delta G_0^{\ddagger}$ in TS, and $\Delta_r G^0$ values of the reoxidation processes.

| Reacting species | *M* | TS distance / Å | $\Delta G_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta H_0^{\ddagger}$ / kJ mol$^{-1}$ | $\Delta_r G_0$ / kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| $Z9GO_5H^{\cdot} + O_2$ | 2 | 1.105 | 155.40 | 161.41 | 160.91 |
| | 4 | 1.01 | 196.36 | 206.78 | 195.52 |
| | 6 | 1.025/2.168[a] | 188.70 | 192.36 | 186.41 |
| $Z9GO_5H_2 + O_2$ | BS 1 | 1.144 | 114.11 | 113.56 | 92.39 |
| | 3 | 1.138 | 101.16 | 113.19 | 102.20 |
| | 5 | 1.112 | 155.87 | 147.94 | 152.71 |
| $Z9GO_5H_3^{\cdot} + O_2$ | 2 | 1.134 | 112.40 | 113.76 | 101.72 |
| | 4 | 1.127 | 110.57 | 117.96 | 110.17 |
| $Z9GO_5H_4 + O_2$ | BS 1 | 1.246 | 73.38 | 68.94 | 25.90 |
| | 3 | 1.181 | 89.73 | 94.59 | 75.40 |
| $Z8GO_4H^{\cdot} + O_2$ | 2 | 1.12 | 154.17 | 149.46 | 154.67 |
| | 4 | 1.117 | 170.14 | 167.19 | 160.06 |
| | 6 | 1.094/2.059[a] | 154.32 | 157.29 | 148.21 |
| $A8GO_4H^{\cdot} + O_2$ | 2 | 1.201 | 72.01 | 74.65 | 42.10 |
| | 4 | 1.023 | 156.38 | 156.90 | 164.53 |

[a] Reaction passes a quasi TS. The first value corresponds to the decreasing O(dioxygen)-H distance, while the second to the increasing O(phenol)-H distance.

**Table S5**. Energies and spin contamination extent for the clusters considered in the study.

| Spin multiplicity | $M_s/M_{max}$ | Spin contamination ($\langle S^2\rangle$ - $S(S+1)$) | | Relative energy[a] |
|---|---|---|---|---|
| | | Opt[b] | SP[c] | |
| **$Z9GO_5$** | | | | |
| 1 | 0/2 | 1.4 | 2.1 | 0.00 |
| 3 | 1/2 | 1.1 | 1.1 | 11.62 |
| 5 | 2/2 | 0.2 | 0.2 | 3.62 |
| **$Z8GO_4$** | | | | |
| 1 | 0/2 | 1.7 | 2.2 | 8.40 |
| 3 | 1/2 | 0.4 | 1.1 | 0.00 |
| 5 | 2/2 | 0.1 | 0.1 | 1.25 |
| **$A8GO_4$** | | | | |
| 1 | 0/0 | 0 | | 0.00 |

[a] Relative energy (in kJ/mol) with respect to the lowest state.
[b] For optimized geometry
[c] For single-point calculations within the $M_{max}$ geometry

Spin contamination is very interesting point of this research. The idea of the spin contamination effect in this case is mainly based on works by Prof. Zilberberg (*e.g.* I. Zilberberg, S.Ph. Ruzankin, Chem. Phys. Lett. 394 (2004) 165), but expanded from transition metals to conjugated carbon systems with degenerate HOMO.

What happens if one looks into the details of spin contamination value calculation [J. Wang, A.D. Becke, V.H. Smith, J. Chem. Phys. 102 (1995) 3477]? For *N*-electron system

$$\left\langle S^2 \right\rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta + 2\int \Gamma^{\alpha\beta\beta\alpha}\left(\mathbf{r}_1, \mathbf{r}_2 \middle| \mathbf{r}_1, \mathbf{r}_2\right) d\mathbf{r}_1 d\mathbf{r}_2$$

, where $\mathbf{r}_i$ denotes the spatial coordinate of *i*-electron, $\Gamma^{\alpha\beta\beta\alpha}\left(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2\right)$ is the two-particle density matrix, $N_\alpha$ and $N_\beta$ indicate the number of α and β electrons in the system. As emphasized in [J. Wang, A.D. Becke, V.H. Smith, J. Chem. Phys. 102 (1995) 3477], the spin contamination originates from incomplete cancellation of the last two terms.

In application to DFT for Slater determinant constructed from the occupied Kohn– Sham orbitals:

$$\left\langle S^2 \right\rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2}+1\right) + N_\beta - \sum_{i\in\alpha}^{occ}\sum_{j\in\beta}^{occ}\left|\int \psi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)d\mathbf{r}_1\right|^2$$

, where $\psi_i(\mathbf{r})$ and $\varphi_j(\mathbf{r})$ are wavefunctions for α and β Kohn-Sham spin orbitals.

Analyzing the last term, one can see that any region with negative spin sign in BS systems donates into spin contamination value [J. Wang, A.D. Becke, V.H. Smith, J. Chem. Phys. 102 (1995) 3477]. Therefore, any antiferromagneticly coupled electron pair implicitly gives 1.0 to the extent of spin contamination.

One can observe that for the certain spatial conformation of a cluster the number of singly occupied molecular orbitals is constant, *i.e.* a certain number of non-paired electrons is present in a cluster. Those electrons, whose magnetic moments are not compensated, contribute to the overall spin magnetic moment of the cluster $M_s$. Those, whose moments are antiparallel and thus compensate, forming antiferromagnetic system, contribute to the integer part of extent of spin contamination (further denoted as *N*). All magnetic (those on singly occupied molecular orbitals) electrons are localized on weakly overlapping orbitals, so each pair of such electrons with opposite spins contribute 1 to the *N* value from determinant of mean value of $<S^2>$ [I. Zilberberg, S.Ph. Ruzankin, Chem. Phys. Lett. 394 (2004) 165].

Consequently, general formula can be deduced:

$M_s^{\,i} + N^i = \text{const.} = M_s^{\,max}$,

where $M_s^{\,max}$ is a $M_s$ value of the most stable state, while $M_s^{\,i}$ and $N^i$ are $M_s$ and integer part of extent of spin contamination of the considered *i*-state, correspondingly.

Say, we have a 4-fold degenerate HOMO with 4 electrons. In this case system may adopt states with magnetic moment $M_s^{\,i}$=0, 1, 2. If considered with BS approach, the integer part of the spin contamination extent would have values $N^i$=2, 1, 0, respectively. (Within the same geometry, for sure - without structural transformations, see SP spin contamination column in Table S5). So, there is an additive character of the magnetic moment of the system (given by the system multiplicity) and integer part of the spin contamination - their sum is constant within certain geometry upon change of multiplicity. In fact the spin contamination extent is additional descriptor of the system, indicating the number of the antiferromagnetically coupled electronic

pairs within the aromatic MO. We also observed this in our previous paper (V.D. Khavryuchenko, O.V. Khavryuchenko, V.V. Lisnyak, G.H. Peslherbe, Chem. Phys. Lett. 513, (2011) 261) for larger carbon clusters.