# DFT investigation on the synthesis mechanism of vinyl acetate from acetylene and acetic acid catalyzed by ordered mesoporous carbon supported zinc acetate

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Table.S1 Structural parameters of free Zinc Acetate and Zinc Acetate adsorbed on OMC, OMC-CO, OMC-COOH and OMC-OH[a]

| Structural parameter | Free $Zn(OAc)_2$ | $Zn(OAc)_2$ on OMC | $Zn(OAc)_2$ on OMC-CO | $Zn(OAc)_2$ on OMC-COOH | $Zn(OAc)_2$ on OMC-OH |
|---|---|---|---|---|---|
| D(Zn-O1)/Å | 2.05 | 2.04 | 2.09 | 2.33 | 2.08 |
| D(Zn-O2)/Å | 2.05 | 2.06 | 2.06 | 2.07 | 2.20 |
| D(Zn-O3)/Å | 2.05 | 2.04 | 2.12 | 2.09 | 2.06 |
| D(Zn-O4)/Å | 2.05 | 2.06 | 2.08 | 2.04 | 2.09 |
| T(O1,O2,O3,O4)/° | 84.3 | 92.8 | 55.6 | 24.3 | 117.9 |
| D(Zn-OMC)/Å | - | 4.0 | 2.32 | 2.10 | 2.17 |

[a]: *The four O atoms of zinc acetic are named O1, O2, O3 and O4 respectively according to clockwise in top view and the following discussion will be described according to this numbering*

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Table.S2 Structural parameters of CHCH adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$[a]

| Structural parameter | Free $C_2H_2$ | $C_2H_2$ on OMC-$Zn(OAc)_2$ | $C_2H_2$ on OMC-CO-$Zn(OAc)_2$ | $C_2H_2$ on OMC-COOH-$Zn(OAc)_2$ | $C_2H_2$ on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|---|
| D(C1-C2)/Å | 1.21 | 1.22 | 1.21 | 1.21 | 1.21 |
| D(C1-H1)/Å | 1.07 | 1.07 | 1.00 | 1.00 | 1.07 |
| D(C2-H2)/Å | 1.07 | 1.07 | 1.00 | 1.00 | 1.07 |
| D(C1-Zn)/Å | - | 2.58 | 3.08 | 3.08 | 4.482 |
| D(Zn-O1)/Å | - | 2.12 | 2.08 | 2.08 | 2.05 |
| D(Zn-O2)/Å | - | 2.06 | 2.10 | 2.10 | 2.00 |
| D(Zn-O3)/Å | - | 2.12 | 2.08 | 2.08 | 3.13 |
| D(Zn-O4)/Å | - | 2.05 | 2.11 | 2.11 | 2.09 |
| D($C_2H_2$-Zn)/Å | - | 2.58 | 3.08 | 3.08 | 4.48 |
| T(O1,O2,O3,O4)/° | - | 148.20 | 169.1 | 172.91 | 122.19 |

[a]: *We name the atom of CHCH according to the following rule: after producing vinyl acetate, the C atom and H atom of ≡CH which turns into –CH2 are named as C1 and H1, the other C atom and Ha atom are named as C2 and H2. The following discussion will be described according to this numbering.*

Table.S3. Structural parameters of $CH_3COOH$ adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$[a]

| Structural parameter | Free $CH_3COOH$ | $CH_3COOH$ on OMC-$Zn(OAc)_2$ | $CH_3COOH$ on OMC-CO-$Zn(OAc)_2$ | $CH_3COOH$ on OMC-COOH-$Zn(OAc)_2$ | $CH_3COOH$ on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|---|
| D(C-Oa)/Å | 1.22 | 1.25 | 1.26 | 1.27 | 1.26 |
| D(C-Ob)/Å | 1.37 | 1.32 | 1.31 | 1.30 | 1.31 |
| D(Zn-Oa)/Å | - | 2.11 | 2.07 | 2.00 | 2.06 |
| D(Zn-O1)/Å | - | 2.03 | 2.97 | 3.10 | 2.99 |
| D(Zn-O2)/Å | - | 2.09 | 2.06 | 3.42 | 1.98 |
| D(Zn-O3)/Å | - | 2.06 | 2.07 | 2.03 | 3.11 |
| D(Zn-O4)/Å | - | 2.32 | 1.92 | 1.94 | 1.93 |

[a]: *We number the carbonyl oxygen of $CH_3COOH$ as Oa and the hydroxyl oxygen of which as Ob. The following discussion will be described according to this numbering*

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**Optimized structures of intermediates involved in the two mechanisms**

**CHCH+$CH_3COOH$**

(1) OMC-$Zn(OAc)_2$

The optimized co-adsorption structure of acetylene and acetic acid on OMC-$Zn(OAc)_2$ is illustrated in Fig. S1 (a). From the calculation result we can find that, when acetylene and acetic acid co-adsorb on the catalyst surface, the distance between acetylene and zinc acetate is rather far, with a value of 4.80 Å. A Zn-O bond forms between acetic acid and zinc acetate, with a length of 2.09 Å. The co-adsorption energy $E_{ads}$(CHCH+$CH_3COOH$) is calculated as -0.748 eV.

(2) OMC-CO-$Zn(OAc)_2$

The energy-lowest structure of co-adsorption structure of acetylene and acetic acid on OMC-CO-$Zn(OAc)_2$ is shown in Fig.S1 (b) and the detailed parameters can be seen in Table.S1. From the data in Table.S1 we can find that the adsorption site of acetylene is far from acetic acid. The distances between centroid of acetylene and the two O atoms in acetic acid are 6.78 Å and 5.87 Å respectively. There is no complex forming after co-adsorbing. The co-adsorption energy $E_{ads}$(CHCH+$CH_3COOH$) is calculated as -0.676 eV

(3) OMC-COOH-$Zn(OAc)_2$

The co-adsorption structure on OMC-COOH-$Zn(OAc)_2$ can be seen in Fig.S1(c). Similar with the former conditions, acetylene adsorbs far from zinc acetate and acetic acid. A Zn-O bond appears between Zn atom and the O atom in carboxyl, with a length of 1.980. The co-adsorption energy $E_{ads}$(CHCH+$CH_3COOH$) is calculated as -0.975 eV.

(4) OMC-OH-$Zn(OAc)_2$

From the optimized structure in Fig.S1 (d) we can find that two Zn-O bonds in zinc acetate break producing similar structures with adsorbed acetic acid. The distance between acetylene and acetic acid is still very far. The detailed structural parameters are shown is Table.S1. The co-adsorption energy $E_{ads}$(CHCH+$CH_3COOH$) in this case is calculated as -0.898 eV.

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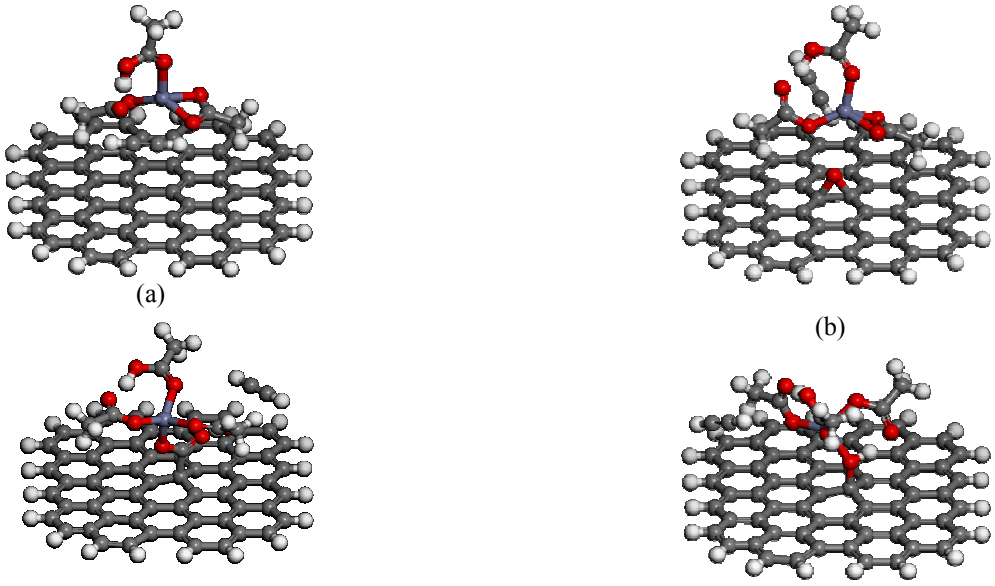



Fig.S1 Optimized model of CHCH and $CH_3COOH$ co-adsorbed on (a) OMC -$Zn(OAc)_2$; (b) OMC-CO-$Zn(OAc)_2$; (c) OMC-COOH-$Zn(OAc)_2$; (d) OMC-OH-$Zn(OAc)_2$; White ball: H atom; Red ball: O atom; Grey ball: C atom; Blue ball: Zn atom

Table S4 Structural parameters of CHCH and $CH_3COOH$ co-adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$

| Parameter | CHCH and $CH_3COOH$ co-adsorbed on OMC-$Zn(OAc)_2$ | CHCH and $CH_3COOH$ co-adsorbed on OMC-CO-$Zn(OAc)_2$ | CHCH and $CH_3COOH$ co-adsorbed on OMC-COOH-$Zn(OAc)_2$ | CHCH and $CH_3COOH$ co-adsorbed on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|
| D(CHCH-Oa)/Å | 5.15 | 6.78 | 5.20 | 5.47 |
| D(CHCH-Ob)/Å | 4.29 | 5.87 | 4.22 | 4.55 |
| D(C1-Zn)/Å | 4.80 | 6.32 | 5.40 | 6.33 |
| D(CHCH-slab)/Å | 5.16 | 4.67 | 4.53 | 5.51 |

**$CH_3COO^{-*}+H^+$**

(1) OMC-$Zn(OAc)_2$

The co-adsorption structure of CH3COO-* and H+ is shown in Fig.S4 (a). We can find that when the H atom dissociates from acetic acid, both of the remaining two O atoms bond to Zn atom, with a lengths of 2.17 Å and 2.16 Å. The specific parameters are shown in Table.S4. The co-adsorption energy $E_{ads}(CH_3COO^{-*}+H^+)$ is calculated as -4.75 eV.

(2) OMC-CO-$Zn(OAc)_2$

The energy-lowest structure in this case is shown in Fig.S4 (b). The structure is similar with that on OMC-Zn(OAc)2. The two atoms of acetic acid bond to Zn atom after H atom dissociating. All of the four Zn-O bonds in zinc acetate enlarges from 2.04 Å, 2.06 Å, 2.04 Å, 2.06 Å to 2.14 Å, 2.16 Å, 2.15 Å, 2.17 Å. The co-adsorption energy $E_{ads}(CH_3COO^{-}{}_{*}+H^+)$ is calculated as -3.82 eV。

(3) OMC-COOH-$Zn(OAc)_2$

On OMC-COOH-$Zn(OAc)_2$, it is a bit different from other cases, since if the H atom of adsorbed acetic acid dissociates, the energy of the system is -3474.05 Ha while if the H atom of the acetate species in zinc acetate dissociates, the total energy is lower as -3474.07 Ha (when acetic acid adsorbs on OMC-COOH-$Zn(OAc)_2$, the H atom of carboxyl will shift and connects to O atom of Zinc acetate generating an acetate species, as discussed above). Therefore, we choose the later structure, see Fig.S4(c). We can find that after H atom dissociating from O atom of zinc acetate, this O atom return to bond with Zn atom, generating a bond with a length of 1.93 Å. The detailed parameters are shown in Table.S4. The co-adsorption energy $E_{ads}(CH_3COO^{-*}+H^+)$ is calculated as -6.20 eV.

(4) OMC-OH-$Zn(OAc)_2$

The energy-lowest structure of this case is shown in Fig.S4(d). After geometry optimization, the two O atoms of acetic acid bond with Zn atom, with lengths of 2.22 Å 和 2.08 Å. The dissociated H atom adsorbs far from the system. The detailed parameters can be seen in Table S4. The co-adsorption energy $E_{ads}(CH_3COO^{-*}+H^+)$ is calculated as -4.28 eV.

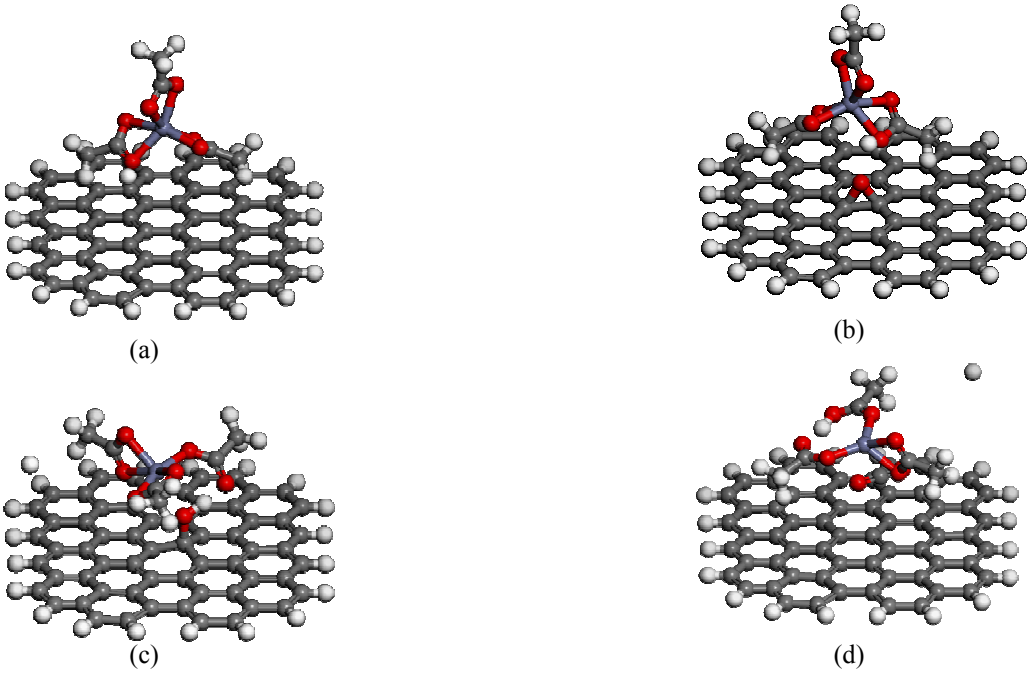



Fig.S2 Optimized model of $CH_3COO^{-*}$ and $H^+$ co-adsorbed on (a) OMC -$Zn(OAc)_2$; (b) OMC-CO-$Zn(OAc)_2$; (c) OMC-COOH-$Zn(OAc)_2$; (d) OMC-OH-$Zn(OAc)_2$; White ball: H atom; Red ball: O atom; Grey ball: C atom; Blue ball: Zn atom

Table S5 Structural parameters of $CH_3COO^{-*}$ and $H^+$ co-adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$

| Structural parameter | $CH_3COO^{-*}$ and $H^+$ on OMC-$Zn(OAc)_2$ | $CH_3COO^{-*}$ and $H^+$ on OMC-CO-$Zn(OAc)_2$ | $CH_3COO^{-*}$ and $H^+$ on OMC-COOH-$Zn(OAc)_2$ | $CH_3COO^{-*}$ and $H^+$ on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|
| D(Zn-Oa)/Å | 2.15 | 2.17 | 2.17 | 2.22 |
| D(Zn-Ob)/Å | 2.17 | 2.16 | 2.16 | 2.08 |
| D(Ob-H)/Å | 3.78 | 5.70 | 5.70 | 6.16 |
| D(Zn-O1)/Å | 2.13 | 2.14 | 3.20 | 2.18 |
| D(Zn-O2)/Å | 2.16 | 2.16 | 3.22 | 2.04 |
| D(Zn-O3)/Å | 2.14 | 2.15 | 1.93 | 3.30 |
| D(Zn-O4)/Å | 2.17 | 2.17 | 1.96 | 2.10 |

**$CH_2C^+H$**

In order to describe conveniently, we give numbers to atoms in $CH_2C^+H$ as C1 for the carbon connected with one H atom and the other carbon as C2. The H atom bonds to C2 is given the number as H1 and H2, which can be seen in Fig.S5.

(1) OMC-$Zn(OAc)_2$

The adsorption structure of $CH_2C^+H$ on OMC-$Zn(OAc)_2$ is illustrated in Fig. S5 (a). It is obviously that there is no chemical bonding between $CH_2C^+H$, acetic acid and zinc acetate. ∠C1-C2-H1 is calculated as 149.94°. The distance between C1 and ketonic oxygen of the adsorbed acetic acid (now it is acetate species) is 6.10 Å. The adsorption energy is -1.72eV as calculated.

(2) OMC-CO-$Zn(OAc)_2$

In this case, two Zn-O bonds form between zinc acetate and the O atoms of acetate species. ∠C1-C2-H1 is 139.67° after geometry optimization. The length of C1-C2 of $CH_2C^+H$ reaches 1.31 Å. The calculated adsorption energy is -1.53 eV.

(3) on OMC-COOH-$Zn(OAc)_2$

In this case, $CH_2C^+H$ also stays far from zinc acetate and acetate species. The detailed parameters and structure are shown in Table.S5 and Fig.S5 (c). Remarkably, in this case, carboxyl will dissociates from the surface producing carbon dioxide. This phenomenon is correspondence to the loss of functional groups on catalysis support during reaction.

(4) OMC-OH-$Zn(OAc)_2$

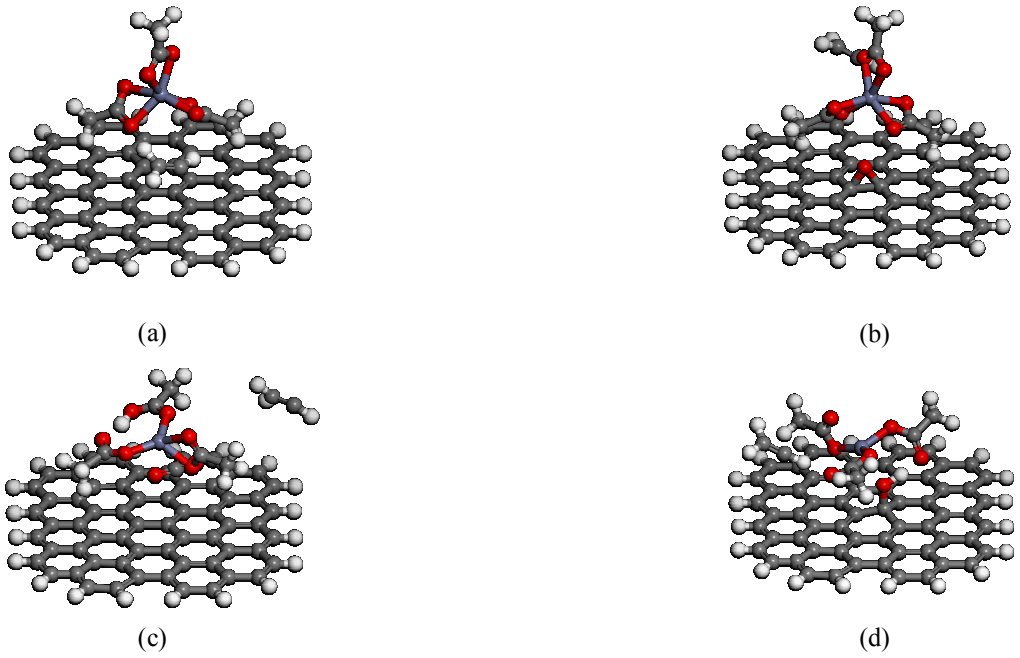



Fig.S3 Optimized model of $CH_2C^+H$ adsorbed on (a) OMC -$Zn(OAc)_2$; (b) OMC-CO-$Zn(OAc)_2$; (c) OMC-COOH-$Zn(OAc)_2$; (d) OMC-OH-$Zn(OAc)_2$; White ball: H atom; Red ball: O atom; Grey ball: C atom; Blue ball: Zn atom

After $CH_2C^+H$ absorbing in this surface, three analogous acetate species are generated, see Fig. S5(d). ∠C2-C1-H1 is calculated as 177.02°. The specific parameters are shown in Table S5. The adsorption energy is calculated as -2.23 eV.

Table S6 Structural parameters of $CH_2=C^+H$ adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$[a]

| Structural parameter | $CH_2=C^+H$ on OMC-$Zn(OAc)_2$ | $CH_2=C^+H$ on OMC-CO-$Zn(OAc)_2$ | $CH_2=C^+H$ on OMC-COOH-$Zn(OAc)_2$ | $CH_2=C^+H$ on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|
| D(C1-C2)/Å | 1.30 | 1.30 | 1.31 | 1.29 |
| D(Oa-C2)/Å | 6.10 | 5.79 | 2.64 | 2.80 |
| D(C2-O3)/Å | 5.51 | 6.17 | 138.67 | 1.98 |
| D(Zn-O1)/Å | 2.15 | 2.15 | 2.07 | 2.04 |
| D(Zn-O2)/Å | 2.15 | 2.16 | 2.08 | 2.02 |
| D(Zn-O3)/Å | 2.16 | 2.14 | 1.92 | 2.27 |
| D(Zn-O4)/Å | 2.17 | 2.18 | 2.16 | 3.28 |

[a]: *Since $CH_2=C^+H$ is generated for CHCH, the numbering rule of $CH_2=C^+H$ is same as that of CHCH, that is, C atom of –CH2 is numbered as C1 and the other C atom is named as C2. The following discussion will be described according to this numbering.*

**$CH_3COOCHCH_2$**[*]

In the previous section, after acetic acid adsorbing, we can find that one or two Zn-O bonds of zinc acetate will break producing acetate species which is similar to acetic acid. Inspired by this

phenomenon, we infer that a replacement of acetate species may exist in the structure of vinyl acetate, which means, the acetate species of vinyl acetate is from zinc acetate, instead of acetic acid. In order to probe into this hypothesis, we take two conditions with and without replacement respectively into consideration.

(1) OMC-$Zn(OAc)_2$

In this condition, we illustrate two adsorption structures of vinyl acetate. In Fig S2 (a), the acetate species of vinyl acetate originates from adsorbed acetic acid and in Fig S2(b), it comes from zinc acetate. The total energy of the former is calculated as -3362.40Ha and that of the later is 3362.41Ha, indicating that the latter is more stable. The detailed structural parameters of the latter are listed in Table S2. Additionally, the adsorption energy of vinyl acetate in Fig.S2 (a) is calculated as -0.264 eV and that in Fig. S2 (b) is -0.311 eV, which further demonstrates our conclusion.

(2) OMC-CO-$Zn(OAc)_2$

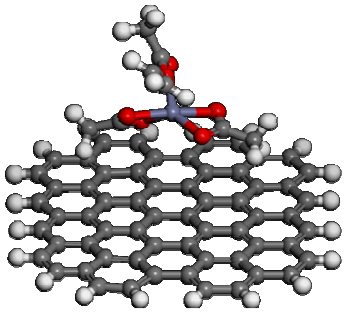
On OMC-CO-$Zn(OAc)_2$ the structure in which acetate species originates from acetic acid is shown in Fig S2.(c) and in Fig.S2 (d), the acetate species is from znic acetate. in Fig.S2 (d), after vinyl acetate adsorbing, Zn atom rebonds with four O atoms, which is similar to the pritine znic acetic. The total energy of the former is -3437.49Ha and that of the later is -3437.50Ha. The adsorption energy of the former is calculated as -0.232 eV and that of the later is -0.246 eV. Thus, we can conclude that the latter is more stable.

(3) OMC-COOH-$Zn(OAc)_2$

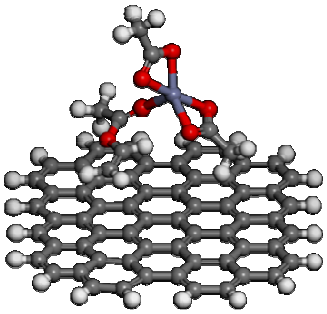
On OMC-COOH-$Zn(OAc)_2$, we also take two conditions into consideration. In Fig. S2(e), the acetate species comes from adsorbed acetic acid while in Fig. S2(f), it originates from znic acetate. The detailed parameters are shown in Table xxx. The absolute value of total energy of the later is large as -3551.43 Ha and that of the former is calculated as -3551.41Ha. The adsorption energy of the later is also higher as -0.395 eV while that of the former is -0.183 eV, which indicates that the structure involved replacement is more stable.

(4) OMC-OH-$Zn(OAc)_2$

In this condition, the two adsorption structures of vinyl acetate are illustrated in Fig. S2(g) and (h). In Fig. S2(g), acetate species of vinyl acetate is originating from acetic acid and in Fig. S2(h), the structure is with a replacement of acetate species. The total energy of the former is -3438.14Ha and that of the later is lower than that as -3438.13Ha, indicating the structure without replacement is more stable. The results of adsorption energies also demonstrate this conclusion as that of the former is -0.218 eV which is much higher than that of the later in absolute value.



(a)



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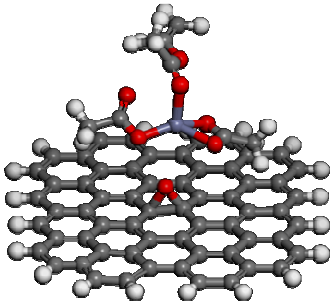

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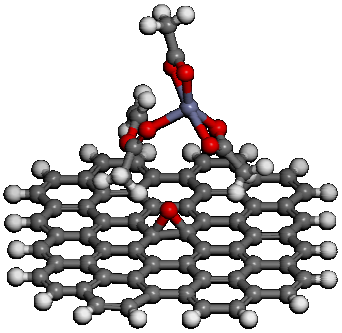
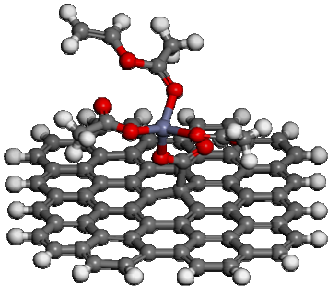
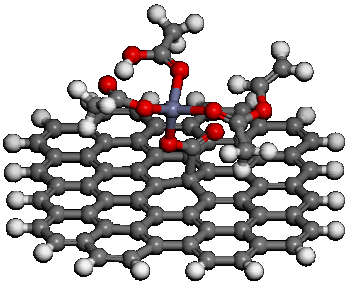


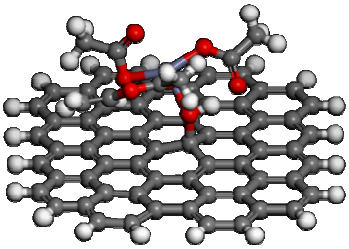
(d)



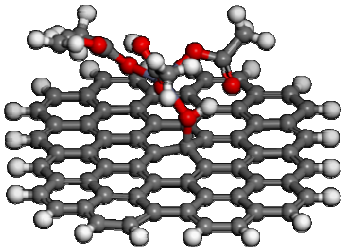
(e)



(f)



(g)



(h)

Fig.S4 Optimized model of $CH_3COOCHCH_2^*$ adsorbed on (a) OMC -$Zn(OAc)_2$ without $CH_3COO^-$ replacement; (b) OMC-$Zn(OAc)_2$ with $CH_3COO^-$ replacement; (c) OMC-CO-$Zn(OAc)_2$ without $CH_3COO^-$ replacement; (d) OMC-CO-$Zn(OAc)_2$ with $CH_3COO^-$ replacement; (e) OMC-COOH-$Zn(OAc)_2$ without $CH_3COO^-$ replacement; (f) OMC-COOH-$Zn(OAc)_2$ with $CH_3COO^-$ replacement; (g) OMC-OH-$Zn(OAc)_2$ without $CH_3COO^-$ replacement; (h) OMC-OH-$Zn(OAc)_2$ with $CH_3COO^-$ replacement;White ball: H atom; Red ball: O atom; Grey ball: C atom; Blue ball: Zn atom

Table S7 Structural parameters of the energy-lowest absorbed vinyl acetate on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$[a]

| Structural parameter | $CH_2$=CH-$OCOCH_3$* on OMC-$Zn(OAc)_2$ | $CH_2$=CH-$OCOCH_3$* on OMC-CO-$Zn(OAc)_2$ | $CH_2$=CH-$OCOCH_3$* on OMC-COOH-$Zn(OAc)_2$ | $CH_2$=CH-$OCOCH_3$* on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|
| D(C1-C2)/Å | 1.33 | 1.33 | 1.33 | 1.33 |
| D(C3-C4)/Å | 1.50 | 1.49 | 1.49 | 1.49 |
| D($O_A$-C2)/Å | 1.40 | 1.40 | 1.40 | 1.40 |
| D($O_A$-C3)/Å | 1.35 | 1.35 | 1.35 | 1.35 |
| D($O_B$-C3)/Å | 1.23 | 1.22 | 1.23 | 1.22 |
| D(Zn-$O_B$)/Å | 2.18 | 2.14 | 2.18 | 2.14 |

[a]: *We number the O atom of C-O-C of vinyl acetate as $O_A$ and the other O atom as $O_B$. The following discussion will be described according to this numbering.*

**Dissociated $CH_3COOCHCH_2$**

(1) OMC-$Zn(OAc)_2$

The optimized structure of dissociated $CH_3COOCHCH_2$ is illustrated in Fig. S3(a) and the structure parameters are shown in Table.S3. We can find that after dissociating, zinc acetate and $CH_3COOCHCH_2$ return to the structure which is similar to the state before reaction. The torsion angle in zinc acetate in this case is 85.4°, similar to that in free zinc acetate as 84.30°.The adsorption energy is calculated as -0.0157 eV, indicating CH3COOCHCH2 is dissociated.

(2) OMC-CO-$Zn(OAc)_2$

From the optimized structure in this case, we can find that the distance between vinyl acetate and zinc acetate is rather far. After desorption of vinyl acetate, four Zn-O bonds reforms in znic acetate with lengths of 2.00 Å, 2.07 Å, 2.16 Å, 2.07 Å, which is almost same with the state before reaction. However, compared with zinc acetate on OMC-CO before reaction, the torsion angle of zinc acetate in this case enlarges from 55.55° to 76.82°, which is due to the long distance between carbonyl and zinc acetate and the interaction between them becomes weaker. The adsorption energy is calculated as -0.00546eV.

(3) OMC-COOH-$Zn(OAc)_2$

The optimized structure of dissociated $CH_3COOCHCH_2$ adsorbing on OMC-COOH-$Zn(OAc)_2$ is shown in Fig. S3. Compared with acetic acid adsorbing on zinc acetate in which Zn atom bonds with two O atoms, in this case, three Zn-O bonds forms, with lengths of 3.10 Å, 2.03 Å and 1.94 Å. The other parameters are listed in Table S3. The adsorption energy is calculated as -0.207eV.

(4) on OMC-OH-$Zn(OAc)_2$

After dissociating, both zinc acetate and vinyl acetate almost return to the initial state, which can be seen from Fig.S3 and Table.S3. The calculated adsorption energy is -0.0650eV.

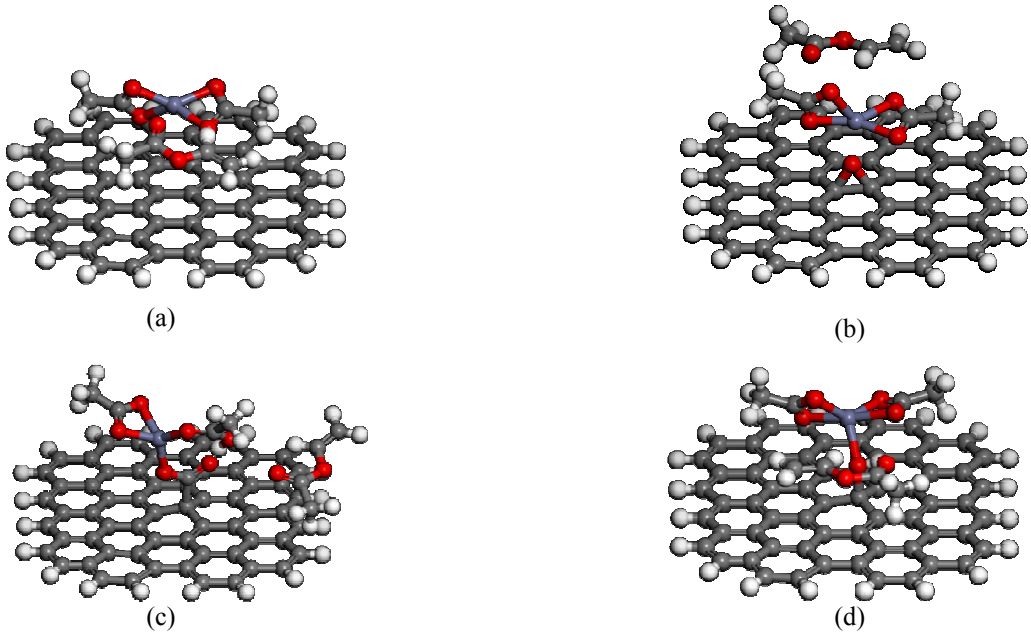



Fig.S5 Optimized model of vinyl acetate adsorbed on (a) OMC -$Zn(OAc)_2$; (b) OMC-CO-$Zn(OAc)_2$; (c) OMC-COOH-$Zn(OAc)_2$; (d) OMC-OH-$Zn(OAc)_2$; White ball: H atom; Red ball: O atom; Grey ball: C atom; Blue ball: Zn atom

Table S8 Structural parameters of vinyl acetate adsorbed on OMC-$Zn(OAc)_2$, OMC-CO-$Zn(OAc)_2$, OMC-COOH-$Zn(OAc)_2$ and OMC-OH-$Zn(OAc)_2$

| Structural parameter | $CH_3COOCHCH_2$ on OMC-$Zn(OAc)_2$ | $CH_3COOCHCH_2$on OMC-CO-$Zn(OAc)_2$ | $CH_3COOCHCH_2$on OMC-COOH-$Zn(OAc)_2$ | $CH_3COOCHCH_2$ on OMC-OH-$Zn(OAc)_2$ |
|---|---|---|---|---|
| D(C1-C2)/Å | 1.33 | 1.33 | 1.33 | 1.33 |
| D(C3-C4)/Å | 1.49 | 1.49 | 1.49 | 1.49 |
| D(O1-C2)/Å | 1.40 | 1.40 | 1.39 | 1.39 |
| D(O1-C3)/Å | 1.35 | 1.35 | 1.38 | 1.38 |
| D(O2-C3)/Å | 1.23 | 1.23 | 1.23 | 1.23 |
| D(Zn-slab)/Å[a] | 4.48 | 8.40 | 1.94 | 2.17 |
| D(Zn-O1)/Å | 2.06 | 2.00 | 2.07 | 2.11 |
| D(Zn-O2)/Å | 2.06 | 2.07 | 3.40 | 2.06 |
| D(Zn-O3)/Å | 2.05 | 2.16 | 2.00 | 2.19 |
| D(Zn-O4)/Å | 2.05 | 2.07 | 2.05 | 2.09 |
| T(O1,O2,O3,O4)/° | 85.40 | 85.40 | 85.40 | 34.10 |

[a]: on OMC-$Zn(OAc)_2$, it is the distance between Zn atom and the carbon slab. On OMC-CO-$Zn(OAc)_2$ ,OMC-$Zn(OAc)_2$ and OMC-$Zn(OAc)_2$, it is the distance between Zn atom and the O atom of the functional group

Table S9 Structural parameters of IS，TS，FS of the steps in Peter Kripylo's mechanism on OMC, OMC-CO, OMC-COOH and OMC-OH

| Catalysis | Reaction | Parameter | IS | TS | FS |
|---|---|---|---|---|---|
| OMC-$Zn(OAc)_2$ | $CH{\equiv}CH+CH_3COOH^*\rightarrow$ | D(C1-Ob)/Å | 4.19 | 2.46 | 1.40 |
| | $CH_2{=}CH\text{-}OCOCH_3{}^*$ | D(C2-Ob)/Å | 4.48 | 2.56 | - |
| | | D(Ob-H3)/Å | 1.03 | 1.26 | - |
| | | D(C2-H2)/Å | 1.07 | 1.07 | 1.09 |
| | | ∠C1-C2-H2/° | 180 | 131.96 | 121.26 |
| | $CH{\equiv}CH\text{-}Zn(OAc)_2\text{-}CH_3COOH$ | D(Zn-OA)/Å | 2.06 | 3.18 | 4.55 |
| | $\rightarrow$ | D(Zn-O1)/Å | 2.04 | 2.07 | 2.06 |
| | $CH_2{=}CHOCOCH_3{+}Zn(OAc)_2$ | D(Zn-O2)/Å | 2.05 | 2.06 | 2.06 |
| | | D(Zn-O3)/Å | 2.06 | 2.06 | 2.05 |
| | | D(Zn-O4)/Å | 2.06 | 2.04 | 2.05 |
| OMC-CO-$Zn(OAc)_2$ | $CH{\equiv}CH+CH_3COOH^*\rightarrow$ | D(C1-Ob)/Å | 4.51 | 2.63 | 1.40 |
| | $CH_2{=}CH\text{-}OCOCH_3{}^*$ | D(C2-Ob)/Å | 3.96 | 2.44 | - |
| | | D(Ob-H3)/Å | 1.11 | 1.34 | - |
| | | D(C2-H2)/Å | 1.07 | 1.08 | 1.09 |
| | | ∠C1-C2-H2/° | 180 | 146.76 | 125.25 |
| | $CH{\equiv}CH\text{-}Zn(OAc)_2\text{-}CH_3COOH$ | D(Zn-$O_A$)/Å | 2.08 | 2.95 | 3.44 |
| | | D(Zn-O1)/Å | 2.05 | 2.05 | 2.06 |
| | $\rightarrow$ | D(Zn-O2)/Å | 2.04 | 2.06 | 2.07 |
| | $CH_2{=}CHOCOCH_3{+}Zn(OAc)_2$ | D(Zn-O3)/Å | 2.04 | 2.06 | 2.09 |
| | | D(Zn-O4)/Å | 2.06 | 2.09 | 2.11 |
| OMC-COOH-$Zn(OAc)_2$ | $CH{\equiv}CH+CH_3COOH^*\rightarrow$ | D(Zn-$O_A$)/Å | 2.12 | 3.16 | 5.68 |
| | | D(Zn-O1)/Å | 3.89 | 2.56 | 2.07 |
| | $CH_2{=}CH\text{-}OCOCH_3{}^*$ | D(Zn-O2)/Å | 3.25 | 3.36 | 3.40 |
| | | D(Zn-O3)/Å | 2.15 | 2.09 | 2.00 |
| | | D(Zn-O4)/Å | 1.95 | 2.03 | 2.05 |
| | $CH{\equiv}CH\text{-}Zn(OAc)_2\text{-}CH_3COOH$ | D(Zn-$O_A$)/Å | 2.12 | 3.16 | 5.68 |
| | | D(Zn-O1)/Å | 3.89 | 2.56 | 2.07 |
| | $\rightarrow$ | D(Zn-O2)/Å | 3.25 | 3.36 | 3.40 |
| | $CH_2{=}CHOCOCH_3{+}Zn(OAc)_2$ | D(Zn-O3)/Å | 2.15 | 2.09 | 2.00 |
| | | D(Zn-O4)/Å | 1.95 | 2.03 | 2.05 |
| OMC-OH-$Zn(OAc)_2$ | $CH{\equiv}CH+CH_3COOH^*\rightarrow$ | D(C1-Ob)/Å | 4.27 | 2.13 | 1.39 |
| | $CH_2{=}CH\text{-}OCOCH_3{}^*$ | D(C2-Ob)/Å | 4.90 | 2.46 | - |
| | | D(Ob-H3)/Å | 1.07 | 1.18 | - |

Continued on next page

Table S9 Structural parameters of IS，TS，FS of the steps in Peter Kripylo's mechanism on OMC, OMC-CO, OMC-COOH and OMC-OH

| | | | | | |
|---|---|---|---|---|---|
| | | D(C2-H2)/Å | 1.07 | 1.06 | 1.09 |
| | | D(C2-H3)/Å | 4.76 | 1.32 | 1.10 |
| | $CH\equiv CH\text{-}Zn(OAc)_2\text{-}CH_3COOH$ | D($Zn\text{-}O_A$)/Å | 2.12 | 2.59 | 3.45 |
| | → | D(Zn-O1)/Å | 3.05 | 2.15 | 2.07 |
| | | D(Zn-O2)/Å | 2.06 | 2.07 | 2.08 |
| | $CH_2=CHOCOCH_3+Zn(OAc)_2$ | D(Zn-O3)/Å | 2.98 | 2.35 | 2.06 |
| | | D(Zn-O4)/Å | 2.07 | 2.06 | 2.05 |

Table S10 Structural parameters of IS，TS，FS of the steps in acid catalyzed mechanism on OMC, OMC-CO, OMC-COOH and OMC-OH

| Catalysis | Reaction | Parameter | IS | TS | FS |
|---|---|---|---|---|---|
| $OMC\text{-}Zn(OAc)_2$ | $CH_3COOH^*\rightarrow CH_3COO^{-*}+H^+$ | D(Zn-Oa)/Å | 2.09 | 2.08 | 2.17 |
| | | D(Zn-O1)/Å | 2.00 | 2.06 | 2.14 |
| | | D(Zn-O2)/Å | 2.09 | 2.11 | 2.16 |
| | | D(Zn-O3)/Å | 2.06 | 2.09 | 2.15 |
| | | D(Zn-O4)/Å | 2.40 | 2.26 | 2.17 |
| | | D(Ob-H) /Å | 1.03 | 2.80 | 5.70 |
| | $CH\equiv CH+H^+\rightarrow CH_2=C^+H$ | D(Ob-H)/Å | 6.028 | 6.52 | 5.64 |
| | | D(C1-H)/Å | 4.62 | 2.84 | 1.11 |
| | | D(C1-C2)/Å | 1.21 | 1.22 | 1.30 |
| | | D(C1-H1)/Å | 1.07 | 1.09 | 1.10 |
| | | ∠C1-C2-H2/° | 180.0 | 160.61 | 149.9 |
| | | ∠C2-C1-H1/° | 178.3 | 143.32 | 123.5 |
| | | ∠C1-C2-H/° | - | - | 121.4 |
| | $CH_2=C^+H+CH_3COO^{-*}\rightarrow$ | D(Zn-O4)/Å | 2.17 | 3.44 | 3.90 |
| | $CH_2=CH\text{-}OCOCH_3{}^*$ | D(C2-O4)/Å | 6.43 | 2.90 | 2.17 |
| | | D(C1-C2)/Å | 1.30 | 1.29 | 1.40 |
| | | D(Zn-Oa)/Å | 2.17 | 2.16 | 2.14 |
| | | D(Zn-Ob)/Å | 2.16 | 2.10 | 2.06 |
| | | D(Zn-O1)/Å | 2.15 | 1.97 | 2.18 |
| $OMC\text{-}CO\text{-}Zn(OAc)_2$ | $CH_3COOH^*\rightarrow CH_3COO^{-*}+H^+$ | D(Zn-Oa)/Å | 2.10 | 2.11 | 2.17 |
| | | D(Zn-O1)/Å | 2.09 | 2.11 | 2.16 |
| | | D(Zn-O2)/Å | 2.02 | 2.09 | 2.14 |
| | | D(Zn-O3)/Å | 2.37 | 2.22 | 2.17 |
| | | D(Zn-O4)/Å | 2.06 | 2.10 | 2.13 |

Table S10 Structural parameters of IS，TS，FS of the steps in acid catalyzed mechanism on OMC, OMC-CO, OMC-COOH and OMC-OH

| | | | | | |
|---|---|---|---|---|---|
| | | D(Ob-H)/Å | 1.04 | 2.51 | 3.80 |
| | $CH\equiv CH+H^+\rightarrow CH_2=C^+H$ | D(Ob-H)/Å | 8.97 | 6.44 | 5.77 |
| | | D(C1-H)/Å | 6.76 | 2.81 | 1.10 |
| | | D(C1-C2)/Å | 1.21 | 1.22 | 1.29 |
| | | D(C1-H1)/Å | 1.07 | 1.10 | 1.10 |
| | | ∠C1-C2-H2/° | 179.0 | 165.3 | 161.9 |
| | | ∠C2-C1-H1/° | 178.4 | 132.8 | 122.2 |
| | | ∠C1-C2-H/° | - | - | 123.0 |
| | $CH_2=C^+H+CH_3COO^{-*}\rightarrow$ | D(Zn-O1)/Å | 2.26 | 2.75 | 3.91 |
| | $CH_2=CHOCOCH_3{}^*$ | D(C2-O1)/Å | 4.55 | 2.33 | 1.40 |
| | | D(C1-C2)/Å | 1.29 | 1.29 | 1.33 |
| | | D(Zn-Oa)/Å | 2.16 | 2.17 | 2.18 |
| | | D(Zn-Ob)/Å | 2.13 | 2.11 | 2.04 |
| | | D(Zn-O4)/Å | 2.16 | 2.06 | 2.06 |
| OMC-COOH-$Zn(OAc)_2$ | $CH_3COOH^*\rightarrow CH_3COO^{-*}+H^+$ | D(Zn-Oa)/Å | 2.00 | 2.02 | 2.00 |
| | | D(Zn-O1)/Å | 3.10 | 3.20 | 3.24 |
| | | D(Zn-O2)/Å | 3.24 | 3.22 | 2.08 |
| | | D(Zn-O3)/Å | 2.03 | 1.92 | 2.06 |
| | | D(Zn-O4)/Å | 1.94 | 1.96 | 1.93 |
| | | D(O2-H)/Å | 1.06 | 1.08 | 9.579 |
| | $CH\equiv CH+H^+\rightarrow CH_2=C^+H$ | D(Ob-H)/Å | 9.54 | 8.11 | 7.25 |
| | | D(C1-H)/Å | 2.67 | 2.26 | 1.11 |
| | | D(C1-C2)/Å | 1.21 | 1.23 | 1.30 |
| | | D(C1-H1)/Å | 1.07 | 1.08 | 1.10 |
| | | ∠C1-C2-H2/° | 179.28 | 163.40 | 140.80 |
| | | ∠C2-C1-H1/° | 179.90 | 156.96 | 122.92 |
| | | ∠C1-C2-H/° | - | - | 122.31 |
| | $CH_2=C^+H+CH_3COO^{-*}\rightarrow CH_2=CH-$ | D(Zn-O1)/Å | 3.22 | 3.08 | 3.09 |
| | $OCOCH_3{}^*$ | D(C2-O2)/Å | 7.86 | 2.99 | 1.35 |
| | | D(C1-C2)/Å | 1.31 | 1.30 | 1.33 |
| | | D(Zn-Oa)/Å | 2.02 | 1.98 | 2.01 |
| | | D(Zn-Ob)/Å | 3.45 | 3.32 | 3.33 |

Continued on next page

Table S10 Structural parameters of IS，TS，FS of the steps in acid catalyzed mechanism on OMC, OMC-CO, OMC-COOH and OMC-OH

| | | | | | |
|---|---|---|---|---|---|
| | | D(Zn-O2)/Å | 2.07 | 2.90 | 4.08 |
| OMC-OH-Zn(OAc)$_2$ | $CH_3COOH^*\rightarrow CH_3COO^{-*}+H^+$ | D(Zn-O$_a$) /Å | 2.05 | 2.08 | 2.08 |
| | | D(Zn-O$_b$) /Å | 3.31 | 2.75 | 2.23 |
| | | D(Zn-O1) /Å | 2.99 | 2.70 | 2.18 |
| | | D(Zn-O2) /Å | 2.00 | 2.00 | 2.04 |
| | | D(Zn-O3) /Å | 3.13 | 3.19 | 3.30 |
| | | D(Zn-O4) /Å | 1.94 | 1.97 | 2.10 |
| | | D(O$_b$-H) /Å | 1.07 | 3.57 | 6.16 |
| | $CH\equiv CH+H^+\rightarrow CH_2=C^+H$ | D(Ob-H) /Å | 6.28 | 5.51 | 4.77 |
| | | D(C1-H) /Å | 5.23 | 2.87 | 1.10 |
| | | D(C1-C2) /Å | 1.2 | 1.22 | 1.29 |
| | | D(C1-H1) /Å | 1.07 | 1.06 | 1.10 |
| | | ∠C1-C2-H2/° | 179.2 | 175.72 | 177.02 |
| | | ∠C2-C1-H/° | 178.3 | 148.26 | 177.02 |
| | | ∠C1-C2-H/° | - | - | 122.00 |
| | $CH_2=C^+H+CH_3COO^{-*}\rightarrow$ | D(Zn-O1)/Å | 2.27 | 2.04 | 2.26 |
| | $CH_2$=CH-$OCOCH_3^*$ | D(C2-Ob)/Å | 2.79 | 2.23 | 1.40 |
| | | D(C1-C2)/Å | 1.29 | 1.30 | 1.33 |
| | | D(Zn-O2)/Å | 2.02 | 1.99 | 1.96 |
| | | D(Zn-O3)/Å | 3.29 | 3.21 | 3.18 |
| | | D(Zn-O4)/Å | 2.04 | 2.04 | 2.01 |

Table S11 Activated barriers and reaction energies of every elementary steps of acid catalysis mechanism on catalysis with different surface structures

| Elementary step | Catalysis | $E_a$/eV | $E_r$/eV |
|---|---|---|---|
| $CH_3COOH^*\rightarrow CH_3COO^{-*}+H^+$ | OMC-Zn(OAc)$_2$ | 5.12 | 4.83 |
| | OMC-COOH-Zn(OAc)$_2$ | 3.32 | 1.91 |
| | OMC-CO-Zn(OAc)$_2$ | 4.81 | 4.67 |
| | OMC-OH-Zn(OAc)$_2$ | 5.37 | 4.79 |
| $CH\equiv CH+H+\rightarrow CH_2C+H$ | OMC-Zn(OAc)$_2$ | 0.241 | -2.45 |
| | OMC-COOH-Zn(OAc)$_2$ | 0.0395 | -2.45 |

Continued on next page

Table S11 Activated barriers and reaction energies of every elementary steps of acid catalysis mechanism on catalysis with different surface structures

| | | | |
|---|---|---|---|
| | $OMC\text{-}CO\text{-}Zn(OAc)_2$ | 0.674 | -2.36 |
| | $OMC\text{-}OH\text{-}Zn(OAc)_2$ | 0.208 | -2.64 |
| $CH_2=C^+H+CH_3COO^{-*}\rightarrow$ | $OMC\text{-}Zn(OAc)_2$ | 0.111 | -3.46 |
| $CH_2=CHOCOCH_3^*$ | $OMC\text{-}COOH\text{-}Zn(OAc)_2$ | 0.674 | -2.36 |
| | $OMC\text{-}CO\text{-}Zn(OAc)_2$ | 0.286 | -3.15 |
| | $OMC\text{-}OH\text{-}Zn(OAc)_2$ | 0.463 | -2.91 |
| $CH_2=CH\text{-}OCOCH_3^*\rightarrow$ | $OMC\text{-}Zn(OAc)_2$ | 0.639 | 0.316 |
| $CH_2=CH\text{-}OCOCH_3+^*$ | $OMC\text{-}COOH\text{-}Zn(OAc)_2$ | 1.211 | 0.188 |
| | $OMC\text{-}CO\text{-}Zn(OAc)_2$ | 1.037 | 0.212 |
| | $OMC\text{-}OH\text{-}Zn(OAc)_2$ | 0.640 | 0.347 |

Table S12 Activated barriers and reaction energies of every elementary steps of Peter Kripylo mechanism on catalysis with different surface structures

| Elementary steps | Catalysis | $E_a$/eV | $E_r$/eV |
|---|---|---|---|
| | $OMC\text{-}Zn(OAc)_2$ | 2.59 | -1.08 |
| $CH\equiv CH+CH_3COOH^*\rightarrow$ | $OMC\text{-}COOH\text{-}Zn(OAc)_2$ | 2.43 | -1.00 |
| $CH_2=CH\text{-}OCOCH_3^*$ | $OMC\text{-}CO\text{-}Zn(OAc)_2$ | 2.64 | -1.02 |
| | $OMC\text{-}OH\text{-}Zn(OAc)_2$ | 2.61 | -0.894 |
| | $OMC\text{-}Zn(OAc)_2$ | 0.639 | 0.316 |
| $CH_2=CH\text{-}OCOCH_3^*\rightarrow$ | $OMC\text{-}COOH\text{-}Zn(OAc)_2$ | 1.211 | 0.188 |
| $CH_2=CH\text{-}OCOCH_3+^*$ | $OMC\text{-}CO\text{-}Zn(OAc)_2$ | 1.037 | 0.212 |
| | $OMC\text{-}OH\text{-}Zn(OAc)_2$ | 0.640 | 0.347 |