Electronic Supplementary Information (ESI):

# Exploring the methanol decomposition mechanism on Pt<sub>3</sub>Ni(100) surface: a periodic density functional theory study

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## 1. Slab model of $Pt_3Ni(100)$ with $(3 \times 3)$ unit cell



Fig. S1. Slab models of the  $Pt_3Ni(100 \text{ with } (3 \times 3) \text{ surfaces.}$  Atomic color code: yellow, platinum; green, nickel.

#### 2. Detailed descriptions of the structures and sites of the methanol and its intermediates

Adsorption of  $CH_3OH$ .  $CH_3OH$  prefers a Ni top site of  $Pt_3Ni(100)$  surface via donation of the lone-pair electrons from oxygen to the metallic surface (Fig. S2), with an  $E_{ads}$  of -0.81 eV. The C–O bond is inclined at an angle of 25° from the surface normal, and the O–H bond is oriented toward a hollow site, facilitating the binding of  $CH_3OH$  to the surface via the oxygen lone-pair orbital. The large O–surface distance (2.07 Å), as well as small changes in the structure of  $CH_3OH$  upon adsorption, suggest the relatively weak adsorption of  $CH_3OH$  on  $Pt_3Ni(100)$ .

Adsorption of  $CH_xO$  (x = 0-3). The methoxy (CH<sub>3</sub>O) formed from O–H bond scission of CH<sub>3</sub>OH also prefers the Pt–Ni bridge site, with an  $E_{ads}$  of –2.42 eV, which is much greater than that of CH<sub>3</sub>OH due to the abstraction of one H. One effect of the adsorption is substantial stretching of the C–O bond (1.43 Å vs 1.34 Å) of CH<sub>3</sub>O due to electron donation from the metallic 4d orbitals to the  $\pi^*$  orbital of C–O in CH<sub>3</sub>O. The other effect of the adsorption may be CH<sub>3</sub>O binding with Pt<sub>3</sub>Ni(100) via  $\eta^2$ (O) modes. The removal of one H atom from CH<sub>3</sub>O generates formaldehyde (CH<sub>2</sub>O), which is a critical intermediate in CH<sub>3</sub>OH decomposition and synthesis. CH<sub>2</sub>O is apt to adsorb on the Pt–Ni bridge site via the  $\eta^1$ (C)- $\eta^2$ (O) mode, with the O atom binding to Pt and Ni atom while the CH<sub>2</sub> group pointing to a Pt atom. The  $E_{ads}$  is -1.17 eV. Similar to CH<sub>2</sub>O, formyl (CHO) prefers to adsorb on the Pt–Ni bridge site via  $\eta^1$ (C)- $\eta^1$ (O) mode, simultaneously forming Pt–C (1.95 Å) and Ni–O (1.93 Å) bonds. The alloying strengthens the adsorption of CHO, with an  $E_{ads}$  of –3.49 eV.

Adsorption of  $CH_xOH$  (x = 0-2). Hydroxymethyl (CH<sub>2</sub>OH), formed by C–H scission of CH<sub>3</sub>OH, prefers to bond at the Pt–Ni bridge site on Pt<sub>3</sub>Ni(100) via  $\eta^1(C)-\eta^1(O)$  mode with the O atom binding to a Ni atom and the C atom binding with a Pt atom. The C–O axis is parallel to the Pt<sub>3</sub>Ni(100) surface ( $\alpha =$ 90 °), and an  $E_{ads}$  of –2.31 eV is obtained. Although hydroxymethylene (CHOH) has a closed-shell electronic configuration, its CH end is still active and can bind stably at the Pt–Ni bridge site through its C atom (in  $\eta^2(C)$  mode), with a high  $E_{ads}$  of –3.80 eV. Hydroxymethylidyne (COH) also prefers to bind to the Pt–Ni bridge site ( $\eta^2(C)$  mode) through its carbon atom, with an  $E_{ads}$  of –4.17 eV, indicating a strong interaction between the C atom and Pt<sub>3</sub>Ni because the C atoms have no H neighbors. Adsorption of CO and Atomic H. CO interacts with the Pt<sub>3</sub>Ni(100) surface through the carbon atom via  $\eta^2$ (C) mode, forming Pt–C (2.02 Å) and Ni–C (1.87 Å) bonds. The  $E_{ads}$  is –2.14 eV. The H atom prefers the fourfold site with a distance of 0.96 Å to the surface. The  $E_{ads}$  is –2.78 eV.

Adsorption of CH<sub>3</sub> and OH. Methyl (CH<sub>3</sub>), formed by the scission of the C–O bond in CH<sub>3</sub>OH, sits at the Pt top site, with an  $E_{ads}$  of –3.03 eV. The hydroxyl radical adsorbs preferentially on the Pt–Ni bridge site (in  $\eta^2$ (O) mode), and the distances of the oxygen to Pt and Ni are 2.11 and 1.93 Å, respectively. The  $E_{ads}$  is –3.99 eV.

#### 3. Detailed descriptions of each H abstraction from methanol and its intermediates

#### 3.1. The O–H bond scission

*R1. CH*<sub>3</sub>*OH* → *CH*<sub>3</sub>*O* + *H*: The IS is the Ni top adsorbed CH<sub>3</sub>OH, while coadsorbed CH<sub>3</sub>O and H are the FS. In this process, the reaction coordinate begins with an O–H stretch vibration at 3346 cm<sup>-1</sup> and ends with CH<sub>3</sub>O bound through the O atom at Pt–Ni bridge site and H adsorbed to an adjacent Pt–Ni bridge site (step (a) in Fig. S3). The activated O–H distance is elongated from 0.992 Å in the IS to 2.006 Å in the TS (TS1 in Fig. S3). The distance from the C atom to the catalyst surface is 2.67 Å, much shorter than its initial value in CH<sub>3</sub>OH (2.83 Å), which indicates that a portion of the CH<sub>3</sub>O in the TS moves closer to the catalyst surface. Beyond the TS, the CH<sub>3</sub>O formed is left at the Pt–Ni bridge site, while the H atom moves to an adjacent Pt–Ni bridge site. This step has an  $E_a$  of 0.19 eV and is exothermic by –0.42 eV.

*R2.*  $CH_2OH \rightarrow CH_2O + H$ : Hydroxyl H abstraction from CH<sub>2</sub>OH affords coadsorbed formaldehyde and hydrogen. The IS is also selected as the most stable CH<sub>2</sub>OH configuration, and the FS consists of a hydrogen atom at Pt top site and CH<sub>2</sub>O adsorbed on the Pt–Ni bridge site via the  $\eta^1(C)$ - $\eta^1(O)$  mode, as shown in Fig. S3 (step (b)). The TS (TS2 in Fig. S3) is similar to the structure of FS. This step has a small  $E_a$  of 0.18 eV, and the reaction is exothermic by –0.34 eV.

*R3. CHOH*  $\rightarrow$  *CHO* + *H*: The process of dehydrogenation of CHOH to CHO is relatively facile. One hydrogen atom moves away from CHOH by breaking the O–H bond with a reaction barrier (0.41 eV) and the distance of the O and H is 1.875 Å at the TS (TS3 in Fig. S3). The dissociation is exothermic with reaction energy of –0.11 eV.

*R4. COH* → *CO* + *H*: After COH is formed, it may yield the desired final products CO and H via O–H bond scission. This process begins with an O–H stretch vibration at 3600 cm<sup>-1</sup>, and COH forms a bidentate structure through the C atom. After the TS (TS4 in Fig. S3), the O atom moves to the top of the C atom, which forms bonds with the Pt and Ni atoms. The H atom departs from C and adsorbs stably at a Pt–Ni bridge site in the FS. This step has an  $E_a$  of 0.44 eV and is exothermic by –0.88 eV.

#### 3.2. The C–H bond scission

*R5.*  $CH_3OH \rightarrow CH_2OH + H$ : The IS is also the Ni top adsorbed CH<sub>3</sub>OH, while coadsorbed CH<sub>2</sub>OH and H are the FS. In this process, the reaction coordinate begins with an C–H stretch vibration at 3126 cm<sup>-1</sup> and ends with CH<sub>2</sub>OH via  $\eta^1(C)$ - $\eta^1(O)$  mode with the O atom binding to a Ni atom and the C atom binding with a Pt atom and H adsorbed to an adjacent Pt top site (step (a) in Fig. S4). The activated C–H distance is elongated from 1.091 Å in the IS to 2.584 Å in the TS (TS5 in Fig. S4), indicating that the C–H bond becomes weaker in the TS. This step has an  $E_a$  of 0.46 eV and is exothermic by −0.56 eV.

*R6. CH*<sub>2</sub>*OH* → *CHOH* + *H*: For C–H scission, methyl H abstraction from CH<sub>2</sub>OH affords coadsorbed hydroxymethylene and hydrogen. The IS is selected as the most stable CH<sub>2</sub>OH configuration (Pt–Ni bridge), and the FS consists of a hydrogen atom at Pt–Ni bridge site and hydroxymethylene on an adjacent Pt top site, as shown in Fig. S4 (step (b)). In this process, the reaction coordinate begins with an C–H stretch vibration at 3058 cm<sup>-1</sup>. The TS (TS6 in Fig. S4) is formaldehyde-like, with the other hydrogen atom essentially moving straight away from the initial location in the CH<sub>2</sub>OH radical to the final Pt–Ni bridge site. This step has an  $E_a$  of 0.77 eV, and the reaction is exothermic by –0.30 eV.

*R7. CHOH* → *COH* + *H*: After CHOH has been produced on the Pt<sub>3</sub>Ni(100) surface, it can produce COH and H via C–H scission. This step begins with a C–H stretch vibration at 2991 cm<sup>-1</sup> and ends with COH and H (step (c) in Fig. S4), with an  $E_a$  is 0.67 eV, and the reaction is exothermic by –0.23 eV.

*R8.*  $CH_3O \rightarrow CH_2O + H$ : Methyl H abstraction from CH<sub>3</sub>O affords coadsorbed formaldehyde and hydrogen. The IS is selected as the most stable CH<sub>3</sub>O configuration (Pt–Ni bridge), and the FS consists of a hydrogen atom at Pt–Ni bridge site and formaldehyde on an adjacent Pt–Ni bridge site, as shown in Fig. S4 (step (d)), which guarantees that the repulsion between them is smaller. This process begins with a C–H stretch vibration at 2902 cm<sup>-1</sup>. To favor C–H bond activation and scission, the C–O bond inclines and brings the hydrogen atom close to the surface (the angle  $\alpha$  changes from 25° in the IS to 28° in the TS). The TS (TS8 in Fig. S4) is formaldehyde-like, with the other hydrogen atom essentially moving straight away from the initial location in the CH<sub>3</sub>O radical to the final Pt–Ni bridge site, and the formaldehyde part rises from the surface, as indicated by the angle  $\alpha$  of 15° in the FS. This step has a small  $E_a$  of 0.65 eV, and the reaction is exothermic by -0.48 eV.

*R9. CH*<sub>2</sub>*O* → *CHO* + *H*: In the formation of CHO, we use CH<sub>2</sub>O as the IS, CHO as its favorable site (i.e., Pt–Ni bridge site) and hydrogen at the Ni top site as the FS (step (e) in Fig. S4. This process begins with a C–H stretch vibration at 2839 cm<sup>-1</sup>. Since the TS (TS9, Fig. S4) has little change in geometry relative to the IS, this step has a low  $E_a$  (0.49 eV). This step is exothermic, with  $\Delta H$  of –0.07 eV.

*R10. CHO* → *CO* + *H*: The C–H bond scission in formyl begins with a C–H stretch vibration at 2637 cm<sup>-1</sup> and ends with CO and H (step (f) in Fig. S4), with an  $E_a$  is 0.56 eV. In the TS (TS10 in Fig. S4), the C–H bond is elongated, and the departing H atom is located at the adjacent Pt–Ni bridge site. The Ni–O bond is broken at a distance of 3.05 Å, and CHO forms a bidentate structure through the C atom. After the TS, the O atom moves to the top of the C atom, which forms bonds with the Pt and Ni atoms. The H atom departs from C and adsorbs stably at a Pt–Ni bridge site in the FS. This process is exothermic, with  $\Delta H$  of −1.00 eV.

## 3.3. The C–O bond scission

 $R11. CH_3OH \rightarrow CH_3 + OH$ : The adsorbed CH<sub>3</sub>OH species also has a high (1.59 eV) barrier for C–O bond cleavage, which is exothermic by –0.76 eV. After decomposition, CH<sub>3</sub> locates on the top site of Pt atom and OH adsorbs on the Pt–Ni bridge site. (step (a) in Fig. S5)

*R12.*  $CH_2OH \rightarrow CH_2 + OH$ : The C–O bond breaking in CH<sub>2</sub>OH leads to the production of CH<sub>2</sub> and OH. This step has an energy barrier and endothermicity of 1.19 and 0.56 eV. The distance of the scissile C–O bond is 3.000 Å in the transition state (TS12 in Fig. S5), while after dissociation this value change to be 4.349 Å and CH<sub>2</sub>/OH coadsorb at their preferred sites.

*R13.*  $CH_3O \rightarrow CH_3 + O$ : The C–O bond scission in CH<sub>3</sub>O has an  $E_a$  of 1.65 eV. The TS for the C–O bond scission in CH<sub>3</sub>O is depicted in Fig. S5, the length of the cleaving C–O bond is calculated to be 2.013 Å in the transition state. In the final state, CH<sub>3</sub> group located on the Pt site through C, while O group located on the bridge of Pt and Ni atoms.

 $R14. CH_2O \rightarrow CH_2 + O$ : We also perform a similar calculation for the C–O bond scission in CH<sub>2</sub>O. The  $E_a$  is 1.36 eV (TS14 in Fig. S5), which is much higher than that of the C–H bond-breaking reaction, suggesting this step is not a possible pathway in CH<sub>3</sub>OH decomposition. To the best of our knowledge, there is no experimental result confirming the existence of the CH<sub>2</sub> species in methanol decomposition.



**Fig. S2.** The most stable adsorption configurations of  $CH_3OH$  and its intermediates involved in  $CH_3OH$  decomposition on the  $Pt_3Ni(100)$  surface. Atomic color code: yellow, platinum; green, nickel; gray, carbon; red, oxygen; and white, hydrogen.

#### (a) CH3OH $\rightarrow$ CH3O + H



(b) CH<sub>2</sub>OH $\rightarrow$ CH<sub>2</sub>O + H



(c) CHOH  $\rightarrow$  CHO + H



**Fig. S3.** The structures of the IS, TS, and FS for each elementary step of O–H bond scission in CH<sub>3</sub>OH. Atomic color code: yellow, platinum; green, nickel; gray, carbon; red, oxygen; and white, hydrogen.

### (a) CH<sub>3</sub>OH $\rightarrow$ CH<sub>2</sub>OH + H



(b)  $CH_2OH \rightarrow CHOH + H$ 







CHOH + H

(c) CHOH $\rightarrow$  COH + H





TS7



COH + H

(d) CH<sub>3</sub>O  $\rightarrow$  CH<sub>2</sub>O + H

CHOH



(e)  $CH_{2}O \rightarrow CHO + H$ 





(f) CHO  $\rightarrow$  CO + H

TS9





Fig. S4. The structures of the IS, TS, and FS for each elementary step of O–H bond scission in CH<sub>3</sub>OH. Atomic color code: yellow, platinum; green, nickel; gray, carbon; red, oxygen; and white, hydrogen.

(a) CH<sub>3</sub>OH  $\rightarrow$  CH<sub>3</sub> + OH



**Fig. S5.** The structures of the IS, TS, and FS for each elementary step of O–H bond scission in CH<sub>3</sub>OH. Atomic color code: yellow, platinum; green, nickel; gray, carbon; red, oxygen; and white, hydrogen.