Supplementary Material

A new and different insight into the promotion mechanisms of Ga for carbon dioxide hydrogenation to methanol over Ga doped Ni(211) bimetallic catalyst

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Table S1. The activation barriers and reaction energies of elementary steps on Ni(211) and Ga-Ni(211) surfaces

<table>
<thead>
<tr>
<th>No.</th>
<th>reaction</th>
<th>Ni(211)</th>
<th>Ga-Ni(211)</th>
<th>Ga\textsubscript{3}Ni\textsubscript{3}(111)</th>
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<td></td>
<td></td>
<td>$E_a$</td>
<td>$E_{ZPE}$</td>
<td>$\Delta E$</td>
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<tr>
<td>R1</td>
<td>H\textsubscript{2}$\rightarrow$H+H</td>
<td>0.10</td>
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<tr>
<td>R2</td>
<td>CO\textsubscript{2}+H$\rightarrow$bi-HCOO</td>
<td>0.78</td>
<td>0.85</td>
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<tr>
<td>R3</td>
<td>CO\textsubscript{2}+H$\rightarrow$trans-COOH</td>
<td>0.95</td>
<td>0.88</td>
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<tr>
<td>R4</td>
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<td>0.74</td>
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<tr>
<td>R5</td>
<td>bi-HCOO$\rightarrow$mono-HCOO</td>
<td>0.71</td>
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<td>R6</td>
<td>bi-HCOO$\rightarrow$HCO+O</td>
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<td>R9</td>
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<td>0.88</td>
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<td>R11</td>
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<td>0.73</td>
<td>0.60</td>
<td>-0.28</td>
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<tr>
<td>R12</td>
<td>HCOOH$\rightarrow$HCO+OH</td>
<td>0.91</td>
<td>0.87</td>
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<td>R13</td>
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<td>0.59</td>
<td>0.57</td>
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<tr>
<td>R14</td>
<td>H\textsubscript{2}CO+H$\rightarrow$CH\textsubscript{2}OH</td>
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<tr>
<td>R15</td>
<td>H\textsubscript{2}CO+H$\rightarrow$CH\textsubscript{2}O</td>
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<td>0.46</td>
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<td>R16</td>
<td>trans-COOH$\rightarrow$cis-COOH</td>
<td>0.49</td>
<td>0.44</td>
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<td>R17</td>
<td>cis-COOH$\rightarrow$CO+OH</td>
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<td>R19</td>
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<td>R21</td>
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<td>No.</td>
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<td>$E_a$</td>
<td>$E_a^{ZPE}$</td>
<td>$\Delta E$</td>
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<td>R22</td>
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<td>1.12</td>
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<td>$c,c$-COOH→COH+OH</td>
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<td>0.38</td>
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<td>R26</td>
<td>COH+H→HCOH</td>
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<td>0.64</td>
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<td>HCOH+H→CH₂OH</td>
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<td>0.60</td>
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<td>R28</td>
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<td>R29</td>
<td>CH₃O+H→CH₃OH</td>
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<td>R30</td>
<td>O+H→OH</td>
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<td>R31</td>
<td>OH+H→H₂O</td>
<td>1.53</td>
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ZPE denotes zero point energy correction, $E_a$, $E_a^{ZPE}$, $\Delta E$ and $\Delta E^{ZPE}$ are in eV.
Table S2. The reaction rate constants at the temperature of 500-600 K of elementary steps in the process of CO$_2$ hydrogenation to CH$_3$OH.

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<th>$k$/s$^{-1}$</th>
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<th>525K</th>
<th>550K</th>
<th>575K</th>
<th>600K</th>
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<td>1  $\text{H}_2 \rightarrow \text{H} + \text{H}$</td>
<td>1.59E+13</td>
<td>1.57E+13</td>
<td>1.56E+13</td>
<td>1.54E+13</td>
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<td>2  CO$_2$ + H $\rightarrow$ $bi$-HCOO</td>
<td>7.57E+06</td>
<td>1.61E+07</td>
<td>3.20E+07</td>
<td>5.99E+07</td>
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<td>3  CO$_2$ + H $\rightarrow$ $trans$-COOH</td>
<td>2.53E+08</td>
<td>5.23E+08</td>
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<td>4  CO$_2$ + CO + O</td>
<td>3.00E+03</td>
<td>9.05E+03</td>
<td>2.47E+04</td>
<td>6.20E+04</td>
<td>1.44E+05</td>
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<td>5  $bi$-HCOO $\rightarrow$ $mono$-HCOO</td>
<td>8.93E+11</td>
<td>1.02E+12</td>
<td>1.15E+12</td>
<td>1.29E+12</td>
<td>1.44E+12</td>
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<td>6  $bi$-HCOO $\rightarrow$ HCO + O</td>
<td>1.81E-05</td>
<td>1.30E-04</td>
<td>7.84E-04</td>
<td>4.05E-03</td>
<td>1.32E-02</td>
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<td>7  $bi$-HCOO + H $\rightarrow$ H$_2$COO</td>
<td>2.01E-06</td>
<td>1.68E-05</td>
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<td>8  $bi$-HCOO + H $\rightarrow$ HCOOH</td>
<td>7.72E+03</td>
<td>2.31E+04</td>
<td>6.26E+04</td>
<td>1.56E+05</td>
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<td>9  H$_2$COO + H $\rightarrow$ H$_2$COOH</td>
<td>4.51E+08</td>
<td>7.92E+08</td>
<td>1.32E+09</td>
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<td>10 HCOOH + H $\rightarrow$ H$_2$COOH</td>
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<td>11 H$_2$COOH $\rightarrow$ H$_2$CO + OH</td>
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<tr>
<td>12 HCOOH $\rightarrow$ HCO + OH</td>
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<tr>
<td>13 HCO + H $\rightarrow$ H$_2$CO</td>
<td>2.41E+08</td>
<td>3.89E+08</td>
<td>6.01E+08</td>
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<td>14 H$_2$CO + H $\rightarrow$ CH$_2$OH</td>
<td>2.84E+04</td>
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<td>15 H$_2$CO + H $\rightarrow$ CH$_3$O</td>
<td>4.48E+08</td>
<td>7.28E+08</td>
<td>1.13E+09</td>
<td>1.70E+09</td>
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<tr>
<td>16 $trans$-COOH $\rightarrow$ $cis$-COOH</td>
<td>2.08E+08</td>
<td>3.60E+08</td>
<td>5.95E+08</td>
<td>9.43E+08</td>
<td>1.44E+09</td>
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<td>17 $cis$-COOH $\rightarrow$ CO + OH</td>
<td>6.23E+03</td>
<td>1.81E+04</td>
<td>4.78E+04</td>
<td>1.16E+05</td>
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<tr>
<td>18 CO + H $\rightarrow$ COH</td>
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<td>19 CO + H $\rightarrow$ HCO</td>
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<tr>
<td>20 $trans$-COOH + H $\rightarrow$ $t,t$-COOH</td>
<td>2.96E+06</td>
<td>6.05E+06</td>
<td>1.16E+07</td>
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<td>21 $t,t$-COOH $\rightarrow$ $t,c$-COOH</td>
<td>3.27E+09</td>
<td>5.21E+09</td>
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<td>22 $t,c$-COOH $\rightarrow$ $c,c$-COOH</td>
<td>4.43E+08</td>
<td>7.72E+08</td>
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<td>23 $t,c$-COOH $\rightarrow$ CO + OH</td>
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<td>26 COH + H $\rightarrow$ HCOH</td>
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Figure S1. The side views (top) and top views (bottom) of optimized structures of potential intermediates in the process of CH$_3$OH synthesis on Ni(211) surface.
Figure S2. The side views (top) and top views (bottom) of the optimized structures of potential intermediates in the process of CH$_3$OH synthesis on Ga-Ni(211) surface.
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<tr>
<td>$\text{R1.} \text{H}_2 \rightarrow \text{H} + \text{H}$</td>
<td>$\text{R2.} \text{CO}_2 + \text{H} \rightarrow \text{bi-} \text{HCOO}$</td>
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<td>$\text{R3.} \text{CO}_2 + \text{H} \rightarrow \text{trans-} \text{COOH}$</td>
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<td>$\text{R6.} \text{bi-} \text{HCOO} \rightarrow \text{HCO} + \text{O}$</td>
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<td>$\text{R7.} \text{bi-} \text{HCOO} + \text{H} \rightarrow \text{H}_2 \text{COO}$</td>
<td>$\text{R8.} \text{bi-} \text{HCOO} + \text{H} \rightarrow \text{HCOO}_2$</td>
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<td>R9.$\text{H}_2\text{COO}+\text{H} \rightarrow \text{H}_2\text{COOH}$</td>
<td>R10.$\text{HCOOH}+\text{H} \rightarrow \text{H}_2\text{COOH}$</td>
<td>R11.$\text{H}_2\text{COOH} \rightarrow \text{H}_2\text{CO}+\text{OH}$</td>
<td>R12.$\text{HCOOH} \rightarrow \text{HCO}+\text{OH}$</td>
<td>R13.$\text{HCO}+\text{H} \rightarrow \text{H}_2\text{CO}$</td>
<td>R14.$\text{H}_2\text{CO}+\text{H} \rightarrow \text{CH}_2\text{OH}$</td>
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<td>IS</td>
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</table>
Figure S3. The side views (top one) and top views (bottom one) of ISs, TSs and FSs of all the elementary steps that are considered in the process of CO$_2$ hydrogenation to CH$_3$OH on Ni(211) surface.
<table>
<thead>
<tr>
<th>IS</th>
<th>TS</th>
<th>FS</th>
<th>IS</th>
<th>TS</th>
<th>FS</th>
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<td>R9 ( \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{C}=\text{O} )</td>
<td>R9 ( \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{C}=\text{O} )</td>
<td>R9 ( \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{C}=\text{O} )</td>
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<td>R10 ( \text{HCOOH} \rightarrow \text{H}_2\text{COOH} )</td>
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<td>R11 ( \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{CO} )</td>
<td>R11 ( \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{CO} )</td>
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<td>R12 ( \text{HCOOH} \rightarrow \text{HCO} )</td>
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<td>R13 ( \text{HCO} \rightarrow \text{H}_2\text{CO} )</td>
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<td>R14 ( \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} )</td>
<td>R14 ( \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} )</td>
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<td>R15 ( \text{HCO} \rightarrow \text{CH}_3\text{OH} )</td>
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<td>R16 ( \text{trans-COOH} \rightarrow \text{cis-COOH} )</td>
<td>R16 ( \text{trans-COOH} \rightarrow \text{cis-COOH} )</td>
<td>R16 ( \text{trans-COOH} \rightarrow \text{cis-COOH} )</td>
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<tr>
<td>R17</td>
<td>cis-COOH→CO+OH</td>
<td>R18</td>
<td>CO+H→COH</td>
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<td>R19</td>
<td>CO+H→HCO</td>
<td>R20</td>
<td>trans-COOH+H→t,t-COHOH</td>
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<tr>
<td>R21</td>
<td>t,t-COHOH→t,c-COHOH</td>
<td>R22</td>
<td>t,c-COHOH→e,c-COHOH</td>
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<td>R23</td>
<td>t,t-COHOH→CO+OH</td>
<td>R24</td>
<td>t,c-COHOH→COH+OH</td>
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</tbody>
</table>
**Figure S4.** The side views (top one) and top views (bottom one) of ISs, TSs and FSs of all the elementary steps that are considered in the process of CO$_2$ hydrogenation to CH$_3$OH on Ga-Ni(211) surface.
Computational details of micro-kinetic modeling

The site balance of intermediates can be written in the coverage of the species.\textsuperscript{1} Pseudo steady-state approximation\textsuperscript{2} was used to describe the adsorbed surface species, based on the assumption that the production and consumption rate are equal for the species. In addition, the adsorptions of CO\textsubscript{2} and H\textsubscript{2} are assumed to be in equilibrium in the micro-kinetic modeling. The equations are displayed as follows:

\[
\begin{align*}
\theta_{CO_2} + \theta_H + \theta_{trans-COOH} + \theta_{cis-COOH} + \theta_{OH} + \theta_{t,t-COHOH} + \theta_{t,c-COHOH} \\
+ \theta_{c,c-COHOH} + \theta_{HCOH} + \theta_{CH_2OH} + \theta^* &= 1
\end{align*}
\]

(1)

\[
k_3 \cdot \theta_{CO_2} \cdot \theta_H - k_{16} \cdot \theta_{trans-COOH} - k_{20} \cdot \theta_{trans-COOH} \cdot \theta_H = 0
\]

(2)

\[
k_{17} \cdot \theta_{cis-COOH} + k_{23} \cdot \theta_{t,t-COHOH} + k_{24} \cdot \theta_{t,c-COHOH} + k_{25} \cdot \theta_{c,c-COHOH} - k_{31} \cdot \theta_{OH} \cdot \theta_H = 0
\]

(3)

\[
k_{16} \cdot \theta_{trans-COOH} - k_{17} \cdot \theta_{cis-COOH} = 0
\]

(4)

\[
k_{20} \cdot \theta_{trans-COOH} \cdot \theta_H - (k_{21} \cdot \theta_{t,t-COHOH} + k_{23} \cdot \theta_{t,t-COHOH}) = 0
\]

(5)

\[
k_{21} \cdot \theta_{t,t-COHOH} - (k_{22} \cdot \theta_{t,c-COHOH} + k_{24} \cdot \theta_{t,c-COHOH}) = 0
\]

(6)

\[
k_{22} \cdot \theta_{t,c-COHOH} - k_{25} \cdot \theta_{c,c-COHOH} = 0
\]

(7)

\[
k_{23} \cdot \theta_{t,t-COHOH} + k_{24} \cdot \theta_{t,c-COHOH} + k_{25} \cdot \theta_{c,c-COHOH} - k_{26} \cdot \theta_{COH} \cdot \theta_H = 0
\]

(8)

\[
k_{26} \cdot \theta_{COH} - k_{27} \cdot \theta_{HCOH} = 0
\]

(9)

\[
k_{27} \cdot \theta_{HCOH} - k_{28} \cdot \theta_{CH_2OH} = 0
\]

(10)

\[
\theta_{CO_2} = \frac{P_{CO_2} \cdot k \cdot \theta^*}{k_{17} \cdot \theta_H}
\]

(11)

\[
\theta_H = \sqrt{\frac{P_{H_2} \cdot k_{11} \cdot \theta^*}{k_{17} \cdot \theta_H}}
\]

(12)

where \(\theta_x\) represents the coverage rate of x. \(\theta^*\) is the coverage of free site.