Supporting Information

Bimetallic Ru-Mo Phosphide Catalysts for the Hydrogenation of CO$_2$ to Methanol

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Table S1. Surface energy of facets on Ru$_{1}$Mo$_{1}$P and MoP

<table>
<thead>
<tr>
<th>Facet on Ru$<em>{1}$Mo$</em>{1}$P</th>
<th>Surface energy (eV)</th>
<th>Facet on MoP</th>
<th>Surface energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(112)</td>
<td>0.18</td>
<td>(100)</td>
<td>0.07</td>
</tr>
<tr>
<td>(020)</td>
<td>0.15</td>
<td>(001)</td>
<td>0.09</td>
</tr>
<tr>
<td>(211)</td>
<td>0.18</td>
<td>(101)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table S2: Effect of simulation cell size on binding energies (BE, eV) of CO$_{2}$ on the dominant facets of Ru$_{0.8}$Mo$_{1.2}$P (112), Ru$_{1.0}$Mo$_{1.0}$P (112), Ru$_{1.2}$Mo$_{0.8}$P (112), Mo$_{3}$P (321), MoP (101), Ru$_{2}$P (112), and RuP (211)

<table>
<thead>
<tr>
<th>System</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P (original)</td>
</tr>
<tr>
<td>Ru$<em>{0.8}$Mo$</em>{1.2}$P</td>
<td>-2.283</td>
</tr>
<tr>
<td>Ru$<em>{1.0}$Mo$</em>{1.0}$P</td>
<td>-3.114</td>
</tr>
<tr>
<td>Ru$<em>{1.2}$Mo$</em>{0.8}$P</td>
<td>-1.433</td>
</tr>
<tr>
<td>Mo$_{3}$P</td>
<td>-1.151</td>
</tr>
<tr>
<td>MoP</td>
<td>-1.024</td>
</tr>
<tr>
<td>Ru$_{2}$P</td>
<td>-0.741</td>
</tr>
<tr>
<td>RuP</td>
<td>-0.503</td>
</tr>
</tbody>
</table>
Table S3 Effect of zero-point energy (ZPE) correction on CO$_2$ binding energy

<table>
<thead>
<tr>
<th>System</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE without ZPE</td>
</tr>
<tr>
<td>Ru$<em>{0.8}$Mo$</em>{1.2}$P (112)</td>
<td>-2.283</td>
</tr>
<tr>
<td>Ru$<em>{1.0}$Mo$</em>{1.0}$P (112)</td>
<td>-3.114</td>
</tr>
<tr>
<td>Ru$<em>{1.2}$Mo$</em>{0.8}$P (112)</td>
<td>-1.433</td>
</tr>
<tr>
<td>Mo$_3$P (321)</td>
<td>-1.151</td>
</tr>
<tr>
<td>MoP (001) without surface P</td>
<td>-1.024</td>
</tr>
<tr>
<td>Ru$_2$P (112)</td>
<td>-0.741</td>
</tr>
<tr>
<td>RuP (211)</td>
<td>-0.503</td>
</tr>
</tbody>
</table>

Surface Analysis of Metal Phosphides in This Study
The oxidation states of monometallic and bimetallic phosphides were determined using XPS and were deconvoluted with the methods described in the experimental section (Figure S2). The oxidation states of Ru, Mo, and P were found to be near 0 (Table S2). However, due to the charge transfer between the atoms, they bear partial positive or negative charges depending on the flow of electrons. For example, Mo 3d$_{5/2}$ peak was shifted to a higher B.E shift compared to the Mo$^0$ at 227.7 eV, which indicates that Mo would most likely be donating electrons. Meanwhile, the B.E. shifts of P 2p$_{3/2}$ atoms were less than the B.E. shift of P$^0$ (130.0 eV), which suggests that the P receives electron.$^1$ Interestingly, the B.E. shift of Ru 3p$_{3/2}$ in monometallic RuP and Ru$_2$P were 461.8 eV and 461.5 eV respectively. These values are more oxidized compared to the Ru$^0$ in metallic 5% Ru/Al$_2$O$_3$ (461.1 eV). However, the B.E. shift of Ru 3p$_{3/2}$ in bimetallic Ru$_x$Mo$_{2-x}$P for $x = 0.8$, 1.0, and 1.2 were 459.8 eV, 460.0 eV, and 459.7 eV respectively. These B.E. shifts were less than that of Ru$^0$, which suggested that Ru atoms in Ru$_x$Mo$_{2-x}$P could receive electron density. This observation has been reported in Ru- based bimetallic phosphide systems.$^{2-4}$
Figure S1. Cu 2p$_{3/2}$ XP spectra used as a standard for B.E. shifts
Crystal Structure and Element Analysis of Metal Phosphides

Figure S3. Crystal structure of (a) MoP sample, (b) MoP reference pattern PDF 04-002-4743, (c) Mo$_3$P sample, (d) Mo$_3$P reference pattern PDF 03-065-1609, (e) RuP sample, (f) RuP reference pattern PDF 04-004-3077, (g) Ru$_2$P sample, and (h) Ru$_2$P reference pattern PDF 04-004-4140. The Si (111) peak marked with * is shifted to 28.44° 2θ.

Table S4. Elemental composition of monometallic and bimetallic Ru and Mo phosphides by ICP-OES, CO adsorption capacities and surface area of each catalyst.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ru</th>
<th>Mo</th>
<th>P</th>
<th>N$_{CO}$ (μmol/g)</th>
<th>S$_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP</td>
<td>1.01</td>
<td>1.00</td>
<td>28</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>Mo$_3$P</td>
<td>2.99</td>
<td>1.00</td>
<td>24</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>RuP</td>
<td>1.02</td>
<td>1.00</td>
<td>23</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Ru$_2$P</td>
<td>1.98</td>
<td>1.00</td>
<td>25</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>Ru$<em>{0.8}$Mo$</em>{1.2}$P</td>
<td>0.78</td>
<td>1.19</td>
<td>1.00</td>
<td>21</td>
<td>8.9</td>
</tr>
<tr>
<td>Ru$_1$Mo$_1$P</td>
<td>1.00</td>
<td>0.99</td>
<td>1.00</td>
<td>20</td>
<td>7.3</td>
</tr>
<tr>
<td>Ru$<em>{1.2}$Mo$</em>{0.8}$P</td>
<td>1.20</td>
<td>0.78</td>
<td>1.00</td>
<td>24</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure. S4 CO₂ temperature programmed desorption on various catalysts after adsorption at 50 °C

Table S5. XPS B.E. shifts for monometallic and bimetallic Ru and Mo phosphides

<table>
<thead>
<tr>
<th>Materials</th>
<th>XPS B.E. shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru 3p₃/₂</td>
</tr>
<tr>
<td>Metallic Mo</td>
<td>227.7</td>
</tr>
<tr>
<td>Ru/Al₂O₃</td>
<td>461.1</td>
</tr>
<tr>
<td>Mo₃P</td>
<td></td>
</tr>
<tr>
<td>Mo₃P</td>
<td></td>
</tr>
<tr>
<td>RuP</td>
<td>461.8</td>
</tr>
<tr>
<td>Ru₂P</td>
<td>461.5</td>
</tr>
<tr>
<td>Ru₀.₈Mo₁.₂P</td>
<td>459.8</td>
</tr>
<tr>
<td>Ru₁.₀Mo₀.₁P</td>
<td>460.0</td>
</tr>
<tr>
<td>Ru₁.₂Mo₀.₈P</td>
<td>459.7</td>
</tr>
</tbody>
</table>
### Table S6. Binding configuration of CO$_2$ over Ru and Mo based phosphides
(Ru atom is purple; Mo atom is blue; P atom is green)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Top view</th>
<th>Side view</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$<em>{1.0}$Mo$</em>{1.0}$P (112)</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>-3.11</td>
</tr>
<tr>
<td>Ru$<em>{0.8}$Mo$</em>{1.2}$P (112)</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>-2.28</td>
</tr>
<tr>
<td>Ru$<em>{1.2}$Mo$</em>{0.8}$P (112)</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>-1.43</td>
</tr>
<tr>
<td>Mo$_3$P (321)</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>-1.15</td>
</tr>
<tr>
<td>MoP (001) with surface P</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>-0.98</td>
</tr>
<tr>
<td>MoP (001) without surface P</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td>-1.02</td>
</tr>
<tr>
<td>Surface</td>
<td>O1 (Å)</td>
<td>O2 (Å)</td>
<td>C (Å)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>--------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>Ru$<em>{1.0}$Mo$</em>{1.0}$P (112)</td>
<td>1.25</td>
<td>1.65</td>
<td>1.62</td>
</tr>
<tr>
<td>Ru$<em>{0.8}$Mo$</em>{1.2}$P (112)</td>
<td>1.28</td>
<td>1.79</td>
<td>0.92</td>
</tr>
<tr>
<td>Ru$<em>{1.2}$Mo$</em>{0.8}$P (112)</td>
<td>1.89</td>
<td>2.07</td>
<td>1.97</td>
</tr>
<tr>
<td>Mo$_3$P (321)</td>
<td>3.68</td>
<td>2.63</td>
<td>3.12</td>
</tr>
<tr>
<td>MoP (001) with surface P</td>
<td>2.95</td>
<td>3.17</td>
<td>3.04</td>
</tr>
<tr>
<td>MoP (001) without surface P</td>
<td>2.14</td>
<td>2.73</td>
<td>2.23</td>
</tr>
<tr>
<td>Ru$_2$P (112)</td>
<td>3.59</td>
<td>2.67</td>
<td>3.12</td>
</tr>
<tr>
<td>RuP (211)</td>
<td>2.73</td>
<td>2.74</td>
<td>2.73</td>
</tr>
</tbody>
</table>

**Table S7.** Distance between CO$_2$ molecule and surface as well as corresponding bond angle
**Table S8.** Partial charge difference (in magnitude, |e|) in the atoms of CO₂ molecule before and after binding on the surface

| Atom in CO₂ | Ru₁Mo₀₁P (112) | Ru₀₈Mo₁₂P (112) | Ru₁₂Mo₀₈P (112) | MoP (001) with surface P removed |
|-------------|----------------|----------------|----------------|---------------------------------
| O₁          | 1.02           | 0.98           | 0.62           | 0.35                            |
| O₂          | 0.95           | 0.73           | 0.45           | 0.53                            |
| C₁          | 1.93           | 1.71           | 0.64           | 0.24                            |

**Table S9.** CO binding energy in different systems

<table>
<thead>
<tr>
<th>System</th>
<th>CO Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru₁₀Mo₁₀P (112)</td>
<td>-2.24</td>
</tr>
<tr>
<td>MoP (001)</td>
<td>-0.83</td>
</tr>
<tr>
<td>Ru₁₂P (112)</td>
<td>-0.65</td>
</tr>
</tbody>
</table>

**Reference**


