# Bimetallic Ru-Mo Phosphide Catalysts for the Hydrogenation of CO<sub>2</sub> to Methanol

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# Abstract

Metal phosphides have been investigated as promising catalysts for many hydrogenation reactions, including CO<sub>2</sub> reduction. Due to the vast compositional space available to discover active and selective transition metal phosphide catalysts for energy-related reactions, we report a variety of Mo-based and Ru-based phosphide catalysts for the hydrogenation of CO<sub>2</sub> to methanol in 1,4-dioxane (200 °C, 1 MPa CO<sub>2</sub>, and 3 MPa H<sub>2</sub>). We determined that from the monometallic catalysts studied (MoP, Mo<sub>3</sub>P, RuP, and Ru<sub>2</sub>P), MoP and Mo<sub>3</sub>P displayed higher methanol production rates

than RuP or Ru<sub>2</sub>P. However, with the addition of Ru to form bimetallic Ru<sub>X</sub>Mo<sub>(2-X)</sub>P (X= 0.8, 1.0, 1.2), the methanol production rate per CO titrated site increased by three-fold, in comparison to MoP. The combination of X-ray photoelectronic spectroscopy (XPS), density functional theory (DFT), CO<sub>2</sub> temperature programmed desorption (TPD), and hydrogenation experiments of reaction intermediates provided evidence that the combination of Ru and Mo in the bimetallic catalyst provides a favorable interaction with CO<sub>2</sub> through electronic effects to promote hydrogenation towards methanol. Lastly, recycling experiments were performed with Ru<sub>1</sub>Mo<sub>1</sub>P, which showed stable methanol production rates for three consecutive reactions. Overall, this paper showcases the promotional effect associated with bimetallic phosphide catalysts for CO<sub>2</sub> hydrogenation to methanol and provides new directions for catalyst discovery with other metal compositions.

## 1. Introduction

Conversion of CO<sub>2</sub> to value-added chemicals (i.e., methanol, dimethyl ether, ethanol, etc.) has attracted significant attention as a possible route to decrease CO<sub>2</sub> emissions.<sup>1-9</sup> Methanol, in particular, is a platform chemical and can serve as a hydrogen storage material.<sup>10</sup> Methanol is commercially produced through syngas (mostly H<sub>2</sub> and CO) with Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> serving as the catalyst.<sup>11</sup> The same catalyst can also be utilized for methanol synthesis directly from hydrogenation of CO<sub>2</sub>.<sup>3</sup> For example, it was shown that 37% selectivity to methanol can be achieved by using this catalyst at a 20% CO<sub>2</sub> conversion.<sup>12</sup> Further modification of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> has been reported with additional promoters, such as ZrO<sub>2</sub>, to improve both selectivity and stability,<sup>13-15</sup> due to structural and electronic effects.<sup>16-19</sup>

Metal phosphides constitute a diverse class of catalytic materials formed by reaction between phosphorus and transition metals. These materials have been reported as highly active catalysts for hydrodenitrogenation (HDN)<sup>20-22</sup>, hydrodesulfurization (HDS)<sup>20, 23-26</sup> and hydrodeoxygenation (HDO)<sup>27-31</sup>, and they have recently attracted attention in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).<sup>32-39</sup> A recent study discovered MoP-K/SiO<sub>2</sub> was active for methanol synthesis from H<sub>2</sub>/CO/CO<sub>2</sub> or H<sub>2</sub>/CO<sub>2</sub> feeds. <sup>11</sup> In direct CO<sub>2</sub> hydrogenation, methanol, CO and methane were observed to be major products. Density function theory (DFT) calculations and diffuse reflectance infrared spectroscopy (DRIFTS) studies showed formate forms as an intermediate and binds as a monodentate formate rather than a bidentate formate, where the monodentate formate is determined to prevent the deactivation by high formate coverage on Cu catalysts. Remarkably, deactivation of the catalyst was not observed after operation at 4 % conversion for 150 h on stream.<sup>11</sup> However, the surface area normalized activity and selectivity to methanol with MoP-K/SiO<sub>2</sub> were not improved compared to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, even if the MoP was highly dispersed on the support.<sup>11</sup> The methanol selectivity with MoP-K/SiO<sub>2</sub> was significantly lower than the CO selectivity, which suggests modification of the active sites in MoP could result in a more effective catalyst.

As a widely used modification strategy, incorporation of second metal to form bimetallic phosphides has been investigated for many hydrogenation reactions, resulting in a wide range of phase-pure materials whose hydrogenation ability can be optimized by changing the catalyst composition.<sup>28-31, 40-42</sup> For example, Rensel et al.<sup>31</sup> synthesized Fe<sub>x</sub>Mo<sub>2-x</sub>P and discovered that the C-O bond cleavage selectivity in phenol hydrodeoxygenation strongly depends on the Fe/Mo ratio. Computational and experimental evidence revealed that changing bulk composition can alter the surface charge and Lewis acid character, which influenced the C-O bond cleavage ability of the

catalyst. Additionally, a similar synergy between heteroatoms in bimetallic phosphides was observed in Co-Ni and Fe-Ni bimetallic phosphides, where a different metal composition enhanced the HDS activity through modification of the active sites.<sup>43-48</sup> Recent studies have also shown that a Ru<sub>1</sub>Mo<sub>1</sub>P bimetallic catalyst results in a strong promotional effect for the selective hydrogenation of substituted aromatic hydrocarbons.<sup>41, 49</sup> For furfural hydrogenation, the synergistic effect in Ru<sub>1</sub>Mo<sub>1</sub>P increases the adsorption energy of the carbonyl O on surface active sites and accelerates hydrogenation of furfural to furfural alcohol.<sup>49</sup> Similarly, this interaction may be important for methanol synthesis, as CO<sub>2</sub> must adsorb on surface active sites and hydrogenate to form methanol.<sup>5, 6, 11, 50, 51</sup> Therefore, the adsorption strength of C=O may improve activation of CO<sub>2</sub>, stabilize CO species, and facilitate the hydrogenation steps towards methanol.<sup>52, 53</sup>

Therefore, in this study, we investigated  $Ru_XMo_{(2-X)}P(X = 0.8, 1.0, 1.2)$  catalysts for CO<sub>2</sub> hydrogenation to determine 1) if the methanol production rate of MoP be enhanced through incorporation of Ru, 2) how the composition of the Ru-Mo phosphide affects methanol production rates, and 3) if and how the CO<sub>2</sub> binding sites change with the formation of a bimetallic Ru-Mo phosphide. Indeed, we observed a 3-fold increase in methanol production rates with Ru<sub>1</sub>Mo<sub>1</sub>P compared to MoP. We were able to show synergy between Ru and Mo in the bimetallic catalyst, which was optimal in a Ru:Mo ratio of 1:1. These results were confirmed by CO<sub>2</sub> temperature programmed desorption (TPD) experiments that provided evidence of stronger CO<sub>2</sub> binding sites in bimetallic compositions of CO<sub>2</sub> adsorption over metal phosphides, which also showed stronger adsorption of CO<sub>2</sub> on Ru-Mo phosphides compared to the monometallic phosphide analogues. Furthermore, hydrogenation experiments of formic acid (FA), as well as CO and CO/CO<sub>2</sub> mixtures, showed higher methanol production rates with Ru<sub>1</sub>Mo<sub>1</sub>P compared to MoP and

Ru<sub>2</sub>P. Overall, these results provide insight into the structure-performance relationship of monometallic and bimetallic Ru- and Mo-based phosphides for CO<sub>2</sub> hydrogenation to methanol.

## 2. Experimental section

## 2.1 Materials

Citric acid monohydrate (Amresco, 99%), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Alfa Aesar, 99%), (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Amresco, 99%), RuCl<sub>3</sub>·xH<sub>2</sub>O (Oakwood Chemicals, 99%), 1,4-dioxane (ACROS Organics, 99%, water 50 ppm max), formic acid (Alfa Aesar, 97%), d<sub>6</sub>-dimethyl sulfoxide (Alfa Aesar, 99.5% isotopic), CO<sub>2</sub> (Airgas, 99.99%) H<sub>2</sub> (Airgas, 99.999%), N<sub>2</sub> (Airgas, 99.998%), 30% CO in He (Airgas, 99.99%), 1%O<sub>2</sub> in He (Airgas, 99.99%).

## 2.2 Catalyst synthesis

Unsupported monometallic (MoP, Mo<sub>3</sub>P, RuP and Ru<sub>2</sub>P) and bimetallic phosphide catalysts (Ru<sub>x</sub>Mo<sub>2-x</sub>P) were synthesized through a previously reported temperature programmed reduction (TPR) method.<sup>30, 41</sup> Monometallic phosphides were synthesized by dissolving the appropriate amount of citric acid (0.7 x mol of metal) in 50 mL deionized water (18 M $\Omega$ ·cm). The metal precursor (Mo: (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and Ru: RuCl<sub>3</sub>·xH<sub>2</sub>O) was added into the solution followed by addition of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> which served as the P source. For example, synthesis of MoP used 5.3 mmol of citric acid, 1.07 mmol of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, and 7.5 mmol of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>. The solution was mixed for 1 h and dried to ~25 mL with a rotary evaporator. The solution was then calcined at 200°C at a 1°C/min ramp rate for 2 h. The resulting coarse powder was ground to a fine powder and calcined at 550°C for 6 h. The precursor was reduced in 160 mL/min of H<sub>2</sub> for 2 h at 650°C with 5°C/min ramp rate except for Mo<sub>3</sub>P that was reduced at 800°C using a similar  $5^{\circ}$ C/min ramp rate. The resulting powder was passivated under a 160 mL/min flow of 1% O<sub>2</sub>/He for 1 h before it was transferred to the N<sub>2</sub> glove box.

Bimetallic Ru<sub>1</sub>Mo<sub>1</sub>P was synthesized by dissolving citric acid (7 mmol) in 50 mL deionized water. After the citric acid was fully dissolved, 0.72 mmol of  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$  was added to the solution, followed by addition of 5 mmol of RuCl<sub>3</sub>·xH<sub>2</sub>O and 5 mmol of  $(NH_4)_2HPO_4$ . The ratio of the metals was adjusted accordingly to obtain the desired Ru:Mo ratio in the final material (e.g. Ru:Mo = 0.8:1.2 and 1.2:0.8). After 1 h of stirring at room temperature, the solution was dried using rotary evaporator to ~25 mL of solution. The resulting thick solution was subsequently dried in a Lindberg Blue M oven at 200°C for 2 h with a 1°C/min ramp rate. The brown coarse powder was ground and calcined at 550°C for 6 h using a 1°C/min ramp rate. The bimetallic RuMo phosphide precursor was reduced under a H<sub>2</sub> flow (160 mL/min) at 650°C for 2 h with 5°C/min ramp rate. Prior to being transferred to a N<sub>2</sub> glove box for storage, the reduced material was passivated for 1 h with a stream of 1%O<sub>2</sub>/He flowing at 160 mL/min.

#### 2.3 Catalyst Characterization

The crystal structures of the synthesized catalysts were confirmed using powder X-ray diffraction (XRD) with a Bruker D8 Advance Davinci instrument with the following settings: 20- $60^{\circ} 2\theta$ ,  $0.02^{\circ}$  step, 2.5 s dwell time, and 15° rotation with Cu K $\alpha$  X-ray source. PHI VersaProbe II x-ray photoelectron spectroscopy (XPS) was used to study the oxidation state of the material. All of the samples were prepared in the glove box on a carbon tape. Cu-foil was used as a reference material and was shifted to Cu  $2p_{3/2}$  binding energy of 932.6 eV (see Fig. S3).<sup>54, 55</sup> Cu  $2p_{3/2}$  peak was used instead of C 1s peak because the binding energy of C 1s peak at 284.8 eV overlapped

with that of Ru 3d. Prior to the analysis, the samples were sputtered with Ar for 2 mins to remove surface oxidation. As is shown in Fig. S2, the Ru 3p region was deconvoluted to reduced Ru  $3p_{3/2}$ (blue) and Ru 3p<sub>1/2</sub> (green) as well as oxidized Ru 3p<sub>3/2</sub> (magenta) and Ru 3p<sub>1/2</sub> (gray). The same method was applied to deconvolute the Mo 3d region into reduced Mo  $3d_{5/2}$  (blue) - Mo  $3d_{3/2}$ (green) pair and oxidized Mo 3d<sub>5/2</sub> (magenta) - Mo 3d<sub>3/2</sub> (gray) pair. Lastly, P 2p region was deconvoluted to reduced P 2p<sub>3/2</sub> (blue)- P 2p<sub>1/2</sub> (green) pair and oxidized P 2p<sub>3/2</sub> (magenta)- P  $2p_{1/2}$  (green) pair. The bulk material composition was determined with inductively coupled plasma - optical emission spectroscopy (ICP-OES; PerkinElmer Optima 8000) using external calibration curves for each element of interest. The active sites on each of the synthesized materials were quantified via CO-pulse chemisorption on a Micromeritics ChemiSorb 2750. Approximately 0.15 g of the sample was initially pretreated under a 20 mL/min flow of H<sub>2</sub> at 400°C for 2 h, followed by a He sweep for 1.5 h at 400°C. The sample was cooled to 100°C under He flow and pretreated with 20 mL/min of H<sub>2</sub>. CO-pulse injections (0.10 mL) were performed at 35°C under 20 mL/min of He. CO<sub>2</sub> temperature programmed desorption (TPD) experiments were performed on a Quantachrome Autosorb IQ-C-XR Gas Sorption Analyzer with an integrated mass spectrometer for MoP, Ru<sub>1</sub>Mo<sub>1</sub>P, Ru<sub>1.2</sub>Mo<sub>0.8</sub>P, and Ru<sub>0.8</sub>Mo<sub>1.2</sub>P. Prior to CO<sub>2</sub> adsorption, each catalyst was pretreated with pure H<sub>2</sub> at 500 °C for 2 hours to remove any residual surface species from passivation. Helium was then used to purge the system and remove physically adsorbed  $H_2$  at 500 °C for 1 hour. After pretreatment, the sample was cooled to 50 °C, and pure CO<sub>2</sub> was introduced for 1 hour with a flow rate of 40 ml/min. After CO<sub>2</sub> adsorption, Helium was introduced at the same flow rate to remove physically adsorbed CO<sub>2</sub> at 50 °C. By applying a 10°C/min ramp rate, desorption products were detected with a mass spectrometer and quantified using an external calibration curve. The Brunauer-Emmett-Teller (BET) surface area was determined for each of the

materials with a Quantachrome Nova 2200e  $N_2$  physisorption instrument. The sample was degassed under vacuum at 200°C prior to analysis.

#### 2.4 Catalysis Activity Measurement

All the reactions were conducted in a 50 mL batch reactor equipped with a programmable temperature controller and pressure indicator. Similar to reported literature, we used dry 1,4dioxane as a solvent due to the solubility of CO2, H2, water and methanol and the ability to resolve all products on the GC column.<sup>56, 57</sup> For this study, the solvent was not optimized and other solvents may also assist in hydrogen transfer<sup>58, 59</sup> or formation of carbonate species,<sup>60, 61</sup> which may affect the catalytic performance by altering the reaction pathway. For each experiment, 4 ml of 1,4dioxane was used as the solvent. The weight of catalyst in use was tuned based on their CO sites density so that the total amount of CO sites in reactor is 0.6 µmol. In a typical experiment, 1 MPa CO<sub>2</sub> was charged in the reactor at room temperature. The reactor was then heated to the target temperature and liquid was stirred at 690 rpm. H<sub>2</sub> was then charged to desirable pressure, which occurred in less than 2 min. The reaction commenced as hydrogen was introduced into the reactor. The total pressure at 180°C, 200°C and 220°C was around 6.48 MPa (940 psig), 6.75 MPa (980 psig) and 7.17 MPa (1040 psig). For CO hydrogenation, the experiment was conducted similarly except a mixture of  $CO_2$  and 30% CO/He were used. At end of the experiment, the reactor was cooled in ice bath for 30 min, the gas was collected in a sample bag, and the liquid phase was recovered at the bottom of reactor for analysis. The methanol concentration was quantified using an Agilent 7890b GCMS with flame ionization detector by correlation with external calibration curves. The gas phase was also analyzed with an Agilent 7890A GC with TCD detector and Carboxen@1010 PLOT column. Dioxane and methanol were not detected in gas phase, but CO<sub>2</sub>,  $H_2$  and permanent gas products were observed. The methanol formation rate was calculated by

total mole of methanol produced per CO site and time. In formic acid (FA) hydrogenation experiments, the reactor was loaded with 4 ml of anhydrous 1,4-dioxane, the catalyst with total CO sites of 0.6 µmol, and 0.11 g of FA. After purging the reactor with pure N<sub>2</sub>, 1 MPa N<sub>2</sub> and 3 MPa H<sub>2</sub> was charged at room temperature before temperature increases to 200 °C. The initial concentration of formic acid after purging the reactor was determined as 0.596 mol/L by Nuclear Magnetic Resonance (NMR-1H). Methanol was then quantified by GCMS and residual formic acid was measured by NMR-1H (d<sub>6</sub>-dimethyl sulfoxide as solvent) with 1,4-dioxane as internal standard.

## 2.5 DFT Calculations for CO<sub>2</sub> Adsorption on Metal Phosphides

All calculations were performed using VASP 5.4.4 (Vienna *Ab initio* Simulation Package) <sup>62-67</sup> through density functional theory (DFT) <sup>68, 69</sup>. The core electrons are described with the projector augmented waves (PAW) <sup>70</sup> method to solve the Kohn-Sham equations.<sup>69, 71</sup> Geometry optimization was performed using the plane wave basis set with a cutoff energy of 450 eV to ensure high precision. We found that energy cutoff of 450 eV is the good cutoff for the convergence of the total energies, energy differences and structural parameters. The general gradient approximation (GGA) using optB88-vdW functional <sup>72, 73</sup> parameters is employed. This functional performs well in describing the bulk properties of type of systems considered in the present work <sup>28, 31, 49</sup> and can account for nonlocal van der Waals interactions. Spin-polarization was included in all calculations with Gamma point sampling of the Brillouin zone.<sup>74</sup> For the geometry optimization, we used first-order Methfessel-Paxton smearing function<sup>75</sup> with a width of 0.1 eV. We used 1 x 10<sup>-5</sup> eV energy difference as convergence criteria to solve the electronic wave function. All the calculations were carried out until the net forces acting on atoms were smaller than 0.03 eV/Å.

The  $Ru_x Mo_{(2-x)}P$  (x = 0.8, 1.0, 1.2) (112), Mo<sub>3</sub>P (321), MoP (001), Ru<sub>2</sub>P (112), and RuP (211) were modeled with P (2  $\times$  2), P (1  $\times$  1), P (4  $\times$  4), P (2  $\times$  2), and P (2  $\times$  3) surface unit cells and three layered slabs separated by at least 15 Å of vacuum. The atoms in the bottom most layer was fixed at the corresponding bulk positions, and those in the top two layers together with the adsorbate atoms were allowed to relax. Those facets were chosen for computation because recently published article by Bonita et al. has shown that for Ru<sub>x</sub>Mo<sub>(2-x)</sub>P, Mo<sub>3</sub>P, MoP, Ru<sub>2</sub>P, and RuP (112), (321), (101), (112), and (211) plane are the most dominant plane based on their XRD pattern.<sup>49</sup> We calculated the surface energy for various surface projections of Ru<sub>1</sub>Mo<sub>1</sub>P and MoP, as shown in Figure S5. The results show Ru<sub>1</sub>Mo<sub>1</sub>P (112) and MoP (101) are not energetically favorable and less likely to be the most dominant surfaces. However, we observed minimal differences in the calculated CO<sub>2</sub> binding energies of less than 0.1 eV on the various surface facets (Ru<sub>1</sub>Mo<sub>1</sub>P (112) : -3.114 eV; Ru<sub>1</sub>Mo<sub>1</sub>P (020) : -3.085 eV; MoP (101) : -0.92; MoP (001) : -0.98), which do not significantly influence the conclusions from CO<sub>2</sub> adsorption over the different metal phosphides. Therefore, the bulk terminated planes are suitable to qualitatively evaluate the CO<sub>2</sub> adsorption ability of these catalysts. As for MoP, the (001) facet was regarded as most active facet in hydrogen evolution reaction <sup>76</sup> and was studied previously in CO<sub>2</sub> hydrogenation<sup>11</sup>. Therefore, the MoP (001) facet was also chosen as model surface in this work, following previous works on MoP<sup>11, 76</sup>. In order to see the effect of the simulation cell size on the binding energies, we performed simulations while increasing the supercell sizes ( $Ru_XMo_{(2-X)}P(X=0.8, 1.0, 1.2)(112)$ ,  $Mo_3P(321)$ , MoP(101), Ru<sub>2</sub>P (112), and RuP (211) = P (4 × 4), P (2 × 2), P (8 × 8), P (4 × 4), and P (4 × 6)). It was found that binding energies change by  $\leq 0.008$  eV (Table S3). Further, the number of slab layers was tested by increasing the layers to four and five for each system while fixing the bottom two and three layers, respectively. The binding energy changed by only  $\leq 0.005$  eV. Therefore, the three

layered slab model was used to compute the CO<sub>2</sub> binding energy with enough accuracy. The effect of the zero-point vibrational energy contributions was also evaluated and reported in Table S6. To calculate zero-point energies (ZPE), we considered the frequency cutoff as 50 cm<sup>-1</sup> and replaced the lower lying frequencies (below ~ 50 cm<sup>-1</sup>) by normal modes of 50 cm<sup>-1</sup>, as suggested by De Moor et al.<sup>77</sup> The variation was significant for Ru<sub>0.8</sub>Mo<sub>1.2</sub>P (112) and MoP (001) (~ 0.02 and 0.06 eV, respectively) whereas other metal phosphides show negligible change in CO<sub>2</sub> binding energy while including ZPE correction. However, the trend in CO<sub>2</sub> binding energy on different metal phosphides is still remaining same after including the ZPE correction. Therefore, we chose all the binding energies without ZPE corrections for further discussion.

To calculate the binding energy, the following equation was used:

$$BE = E_{ADSORBATE+SURFACE} - E_{ADSORBATE} - E_{SURFACE} \quad (1)$$

The binding energies (denoted as BE) were calculated according to Eqn. (1), wherein  $E_{ADSORBATE+SURFACE}$  is defined as the total energy of species adsorbed on the surface;  $E_{SURFACE}$  is defined the total energy of surface; and  $E_{ADSORBATE}$  is defined as the energy of the adsorbed species on the surface in the gas phase.

#### 3. Results and Discussion

#### 3.1 Catalyst Characterization and Catalytic Assessment for CO<sub>2</sub> Hydrogenation

The evaluation of monometallic and bimetallic phosphides for CO<sub>2</sub> hydrogenation is limited. Molybdenum oxide, nitrate and sulfate have been investigated in CO<sub>2</sub> hydrogenation showing their capability of activation of CO<sub>2</sub> at ambient pressure.<sup>78</sup> Molybdenum-based carbides were also studied and found to be highly active methanol synthesis catalyst, especially in low temperature and liquid-phase condition.<sup>56, 57, 79, 80</sup> Different carbide phases, such as MoC and Mo<sub>2</sub>C, were found to strongly impact the conversion of CO<sub>2</sub> into target products.<sup>80, 81</sup> Recently reported research with metal phosphides have focused on potassium promoted MoP/SiO<sub>2</sub> with comparable methanol yields to the commercial catalyst at 230 °C.<sup>11</sup> However, potassium-free MoP and other Mo<sub>x</sub>P<sub>y</sub> phases have not received the same attention for CO<sub>2</sub> hydrogenation as Mocarbide<sup>56, 57, 79, 82</sup>. Therefore, we started this study by comparing MoP and Mo<sub>3</sub>P to understand the catalytic consequences of bulk composition for methanol synthesis from a CO<sub>2</sub>/H<sub>2</sub> feed.

Both MoP and Mo<sub>3</sub>P were synthesized using a temperature programmed reduction method at 650 °C and 800 °C, respectively. The crystal structure of the as-synthesized samples was confirmed by XRD, as shown in Fig. S1. MoP has a hexagonal WC type structure<sup>83</sup>, and Mo<sub>3</sub>P has a tetragonal structure.<sup>49</sup> The elemental composition was determined by ICP-OES, and the Mo:P ratio was consistent with the nominal bulk composition (Table. S1). As these metal phosphides have different metal to P ratios, the metal site density can vary from sample to sample, we used CO to titrate the metal sites on the various synthesized materials.<sup>57, 84, 85</sup> The CO uptake for the catalysts is presented in Table S1, and the measured values are consistent with previous reports.<sup>30, 86</sup>

In order to evaluate the performance of MoP and Mo<sub>3</sub>P, a 50 ml batch reactor was used with 1,4-dioxane as the solvent at a reaction temperature of 200 °C, which is lower than the typical methanol synthesis condition (250-300 °C) because previous work by Chen et al.<sup>56, 57</sup> showed methanol synthesis from CO<sub>2</sub> hydrogenation can be highly favorable at low temperature (135-200 °C) using 1,4-dioxane as the solvent.<sup>56, 57</sup> The reactor was charged to an initial pressure of 6.75 MPa with a  $P_{H^2}/P_{CO^2} = 3/1$ . To appropriately account for variations in the site density of each material, the amount of catalyst added to each reaction experiment was equivalent to 0.6 µmol of CO titrated sites. The methanol concentration versus time is shown in Fig. 2 (a) as well as the

methanol formation rate per CO titrated site in Fig. 2(b). Both catalysts were active for methanol synthesis, and the CO-sites-normalized methanol production rates ( $r_{\text{MEOH}}$ ) were 0.0004 and 0.0003 s<sup>-1</sup> for Mo<sub>3</sub>P and MoP, respectively.

One approach to enhance the activity of the Mo-phosphide catalysts is through the formation of a bimetallic phosphide by incorporating a second metal, such as Ni, Fe and Ru. This approach has been reported as an effective strategy to improve the selectivity and catalytic activity for hydrogenation and hydrodeoxygenation reactions.<sup>28-31, 41, 49</sup> For example, in our previous work, an enhanced selectivity to furfural alcohol from furfural was observed over Ru<sub>1</sub>Mo<sub>1</sub>P due to the synergy between Ru, Mo and P.<sup>49</sup> The Ru/Mo ratio was able to tune the adsorption of the carbonyl oxygen of furfural on the metal surface, which strongly impacted the resulting hydrogenation ability. Therefore, we synthesized three Ru-Mo bimetallic phosphides (Ru/Mo=0.66, 1 and 1.5) as well as two common phases of ruthenium phosphides (RuP and Ru<sub>2</sub>P) to evaluate their catalytic performance.

The crystal structure of RuP, Ru<sub>2</sub>P and Ru-Mo bimetallic phosphides were confirmed by XRD using Si(111) as an internal standard, as shown in Fig. 1 and Fig. S1. The main features of both bimetallic and monometallic phosphide are consistent to their respective reference pattern. Both RuP and Ru<sub>2</sub>P shares orthorhombic crystal structure<sup>24</sup>. The XRD pattern of RuMoP (Fig. 1) shows a similar pattern to Ru<sub>2</sub>P, suggesting a similar crystal structure of Ru<sub>1.2</sub>Mo<sub>0.8</sub>P, Ru<sub>1</sub>Mo<sub>1</sub>P and Ru<sub>0.8</sub>Mo<sub>1.2</sub>P to Ru<sub>2</sub>P (orthorhombic crystal structure) with (112), (211), and (020) as the most dominant facets. However, we observed a shift to lower angles in the (112) and (211) peak positions of Ru<sub>2</sub>P, Ru<sub>1.2</sub>Mo<sub>0.8</sub>P, Ru<sub>1</sub>Mo<sub>1</sub>P and Ru<sub>0.8</sub>Mo<sub>1.2</sub>P as the Mo content was increased, which indicated the unit cell expanded with Mo incorporation into the crystal lattice. Additionally, phase separation or alternative phases were not observed with the various Ru-Mo compositions. From

ICP-OES analysis (Table S1), the bulk compositions matched the nominal values for each material. The surface area and CO adsorption capacities of each metal phosphide are also included in Table S1.

The effect of Ru incorporation on methanol synthesis was assessed under the same reaction condition as MoP and Mo<sub>3</sub>P. Fig. 2 (a) depicts the methanol synthesis performance of the bimetallic phosphides as the function of time. The bimetallic catalyst with the lowest amount of Ru (Ru<sub>0.8</sub>Mo<sub>1.2</sub>P) produced more methanol than both MoP and Mo<sub>3</sub>P (Fig. 2 (a)). As the Ru/Mo is adjusted to 1, the methanol production rate further increases to ~ 3 times higher than MoP, showing the strong promotional effect of Ru (Fig. 2(b)). After 7 hours of reaction, 18  $\mu$ mol of methanol was produced by Ru<sub>1</sub>Mo<sub>1</sub>P, while less than 4  $\mu$ mol of methanol was produced from Mo<sub>3</sub>P. Interestingly, as the Ru/Mo is increased to 1.5, a decrease in the methanol production rate was observed (Fig. 2(b); Ru<sub>1.2</sub>Mo<sub>0.8</sub>P). The same trend can be observed at various temperatures from 180 °C to 220 °C, as is shown Fig. 3 From these experiments, it is unlikely that the Ru is the primary contributor for the enhanced methanol production.

To exclude the possibility that phase separation and formation of ruthenium phosphide phases causing higher methanol formation rates, we also evaluated the performance of RuP and Ru<sub>2</sub>P (Fig. 2 (a) and (b)). As shown in Fig. 2, both RuP and Ru<sub>2</sub>P have the lowest methanol production rates among all the metal phosphides in this study. Therefore, the co-existence of Mo and Ru sites is critical to enhance methanol production. A similar effect has been observed with other bimetallic catalysts.<sup>56, 57</sup> Chen et al.<sup>57</sup> studied Cu supported on Mo<sub>2</sub>C in methanol synthesis. The synergy between Cu and Mo<sub>2</sub>C provided significant improvement in methanol production at low temperature (135 °C) in the liquid phase. The mechanism was studied theoretically on other supported catalysts, such as Au/titanium carbide (TiC) and Ni doped Cu.<sup>52, 87-89</sup> When a second

metal was incorporated on the support (TiC or Cu), electron transfer can occur between the metals to strengthen the adsorption of reaction intermediates to promote CO bond cleavage of  $CO_2$ .<sup>52, 87-89</sup>



**Figure 1.** (a) Wide-angle XRD patterns of Ru-Mo bimetallic phosphides and (b) an enlarged scale of the XRD patterns between  $2\theta = 36^{\circ}$  and  $43^{\circ}$ 



**Figure 2.** Methanol concentration over various catalyst versus reaction time (a). Methanol formation rates per CO site calculated after five hours (b). The error bars represent the standard error from three experimental measurements.



**Figure 3.** Experimental methanol formation rates after five hours at three different temperatures over Ru-Mo bimetallic phosphides with different Ru/Mo ratios.

#### 3.3 Probing the Nature of Active Sites via Experimental and Theoretical Approaches

To determine if similar electronic effects could exist with the Ru-Mo bimetallic phosphides, we utilized XPS to measure the relative oxidation of Ru and Mo (Fig S2). The binding energy shift of each element is listed in Table 1 and Table S2. As shown in Table. 1, the binding energy of Mo (3d<sub>3/2</sub>) in Mo<sub>3</sub>P, MoP, Ru<sub>0.8</sub>Mo<sub>1.2</sub>P, Ru<sub>1.2</sub>Mo<sub>0.8</sub>P and Ru<sub>1</sub>Mo<sub>1</sub>P was determined as 227.9, 228.1, 228.1, 228.0 and 228.1 eV, respectively. The binding energy of metallic Mo is 227.7

eV, each of the phosphide catalysts exhibit partial positive charge. However, the variation in the Ru-Mo composition does not significantly influence the binding energy of Mo. The same observation was reported in  $(Ni_{l-x}M')_2P$  (M' = Cr, Fe, Co), where the binding energy shift was ~ 0.1 eV for different Ni:M' ratios.<sup>47</sup> The binding energy of Ru in Ru<sub>0.8</sub>Mo<sub>1.2</sub>P, Ru<sub>1.2</sub>Mo<sub>0.8</sub>P and Ru<sub>1</sub>Mo<sub>1</sub>P was 462, 461.8 and 461.5 eV, which suggests negative charge on the Ru due to the lower binding energy compared with Ru<sup>0</sup> (461.1 eV). This is strong evidence of charge polarization in Ru-Mo bimetallic phosphides as we reported in our earlier work.<sup>49</sup> Other catalysts, such as Ru<sub>2</sub>P and RuP, have higher binding energies (461.5 and 461.8 eV) than Ru<sup>0</sup> (461.1 eV) due to charge transfer to neighboring phosphorus atoms. The binding energy of Ru and Mo from each catalyst can be correlated to their CO-site-normalized methanol formation rates. As noted in Table 1, a similar relative oxidation of Mo sites in MoP, Mo<sub>3</sub>P and Ru-Mo bimetallic phosphides were observed, while their activities are very different. Comparably, negative charges accumulated on Ru sites of Ru<sub>0.8</sub>Mo<sub>1.2</sub>P, Ru<sub>1.2</sub>Mo<sub>0.8</sub>P and Ru<sub>1</sub>Mo<sub>1</sub>P and their activities are much higher than Ru<sub>2</sub>P and RuP, whose Ru sites are more positive charged than Ru metal. This evidence suggests a possible correlation between charge polarization and methanol synthesis. Therefore, we also performed DFT calculations on both bimetallic and monometallic phosphides to understand the surface charge distribution through a Bader charge analysis (Table 1). Computationally, the average partial charge on the Mo atoms on the surface followed the order:  $Mo_3P$  (+0.3 lel) <  $Ru_{1,2}Mo_{0,8}P$  (+0.54 lel) < MoP (+0.52 lel) <  $Ru_{0,8}Mo_{1,2}P$  (+0.62 lel) <  $Ru_1Mo_1P$  (+0.70 lel), which shows Mo sites are more positive than metallic Mo atoms. As for the average partial charge on the Ru atoms,  $Ru_{1.2}Mo_{0.8}P(-0.29 \text{ lel}) < Ru_1Mo_1P(-0.23 \text{ lel}) < Ru_{0.8}Mo_{1.2}P(-0.21 \text{ lel}) < Ru_2P(+0.07 \text{ lel})$ < RuP (+0.11 lel), which indicates more average negative charges on Ru sites from Ru-Mo

bimetallic phosphides. This computational result is consistent to the charge polarization we observed on bimetallic phosphides experimentally.

**Table. 1** Binding energies and Bader charges for different atomic species on metal phosphides

 surface, and the overall rate of methanol formation

	Binding Energy (eV)			Surface Charges ( e )			(10.4 1)	
	Ru	Мо	Р	Ru	Мо	Р	$r_{\rm MeOH} (10^{-4} \bullet {\rm s}^{-1})$	
Ru <sub>1</sub> Mo <sub>1</sub> P	460.0	228.1	129.7	-0.23	+0.70	-0.46	9.7	
Ru <sub>0.8</sub> Mo <sub>1.2</sub> P	459.8	228.1	129.7	-0.21	+0.62	-0.41	4.3	
Ru <sub>1.2</sub> Mo <sub>0.8</sub> P	459.7	228.0	129.6	-0.29	+0.54	-0.25	6.4	
Mo <sub>3</sub> P		227.9	129.2		+0.30	-0.91	3.9	
MoP		228.1	129.3		+0.55	-0.55	2.9	
Ru <sub>2</sub> P	461.5		129.7	+0.07		-0.14	2.8	
RuP	461.8		129.7	+0.11		-0.11	0.8	
$Ru/Al_2O_3$	461.1							
Metallic Mo		227.7						

#### 3.4 DFT and TPD Study on CO<sub>2</sub> Adsorption Over Metal Phosphides

In order to understand how the corporation of Ru and Mo sites on metal phosphide influences the catalytic performance for  $CO_2$  hydrogenation, we utilized computational modeling to understand whether  $CO_2$  has stronger interaction with the Ru and Mo sites on bimetallic phosphides than monometallic phosphides, as  $CO_2$  adsorption is the initial step for methanol synthesis. Therefore, the  $CO_2$  binding on metal phosphide surface was modeled via DFT (Table

S3). The structure of  $CO_2$  adsorbed on metal sites were allowed to relax so that the most stable structure was obtained, as is shown in Fig. 4 and Table S4. For bimetallic phosphides, we found that a single  $CO_2$  molecule tends to bind between Mo and Ru sites. (side view: Fig. 4(a-c), top view: Table S4) First oxygen atom (O<sub>1</sub>) stays above the positively charged Mo with perpendicular distance to surface of 1.2~1.9 Å, while the carbon atom also remains close to surface with a distance of 0.9~1.9 Å. The second oxygen atom (O<sub>2</sub>) is farther from the surface due to weaker interactions (perpendicular distance 1.6~2.1 Å). For Ru<sub>1</sub>Mo<sub>1</sub>P and Ru<sub>1.2</sub>Mo<sub>0.8</sub>P, the CO<sub>2</sub> molecule is slightly bent (Fig. 4, O-C-O bond angle is around 175°) while CO<sub>2</sub> on Ru<sub>0.8</sub>Mo<sub>1.2</sub>P shows more significant change in the adsorption configuration (Fig. 4, O-C-O bond angle is 123°). CO<sub>2</sub> adsorption on Mo<sub>3</sub>P, Ru<sub>2</sub>P and RuP surfaces showed a linear configuration, and the distances between each atom from  $CO_2$  and these monometallic phosphide surfaces are farther than the bimetallic phosphide (Fig.4 and Table S4). As for MoP (001) facet, first layer of P was removed so that its metal sites can be accessible to  $CO_2$  molecule as other phosphides in this study. As is shown in Fig. 4, when CO<sub>2</sub> binds on Mo sites, its O-C-O binding angle becomes 130°, indicating strong adsorption of CO<sub>2</sub> over metal sites. In case that P was not removed over MoP (001) facet, the  $CO_2$  molecule showed linear configuration in Table. S4. This indicates that metal sites have stronger interaction with  $CO_2$  than surface P. We also calculated the binding energy of  $CO_2$  on the (112) facet of Ru<sub>x</sub>Mo<sub>(2-x)</sub>P, (321) facet of Mo<sub>3</sub>P, (001) facet of MoP, (112) facet of Ru<sub>2</sub>P, and (211) facet of RuP. It was shown in Table S4 that binding energies of  $CO_2$  over those surfaces of RuP, Ru<sub>2</sub>P, MoP (with surface P), MoP (without surface P) and Mo<sub>3</sub>P are -0.5, -0.74, -0.98, -1.02 and -1.15 eV, respectively, indicating stronger  $CO_2$  adsorption over Mo-based phosphides rather than Ru-based phosphides. According to Tang et al., CO<sub>2</sub> adsorption on Cu (111) is -0.03 eV.<sup>90</sup> In case of other transition metals, the binding energies of  $CO_2$  over Ni (110) and Fe (100) are -0.52 eV

and -1.47 eV, respectively.<sup>91,92</sup> Our calculations show the binding strength of CO<sub>2</sub> over Mo or Ru based phosphides is close to the transition metals. Additionally, as Ru was incorporated to MoP to form Ru<sub>1</sub>Mo<sub>1</sub>P, binding energy of CO<sub>2</sub> increases from -1.02 eV to -3.11 eV (Table S4). Interestingly, the bent configuration of CO<sub>2</sub> on MoP (001) and Ru<sub>0.8</sub>Mo<sub>1.2</sub>P (112) does not result in a higher binding energy than Ru<sub>1</sub>Mo<sub>1</sub>P (112), a surface that binds CO<sub>2</sub> in a linear configuration. The variation in the CO<sub>2</sub> binding configuration could be due to structural or electronic differences in the surfaces. Table S8 showcases the charge transfer between CO<sub>2</sub> and the various surfaces. It is clear that the magnitude of charge transfer between CO<sub>2</sub> and Ru<sub>1</sub>Mo<sub>1</sub>P (112) is larger than other materials, which stabilizes adsorbed CO<sub>2</sub> and results in the highest binding energy on Ru<sub>1</sub>Mo<sub>1</sub>P (112). A similar improvement was also reported with Cu and Au supported on titanium carbide (TiC), when binding energy of CO<sub>2</sub> enlarges from -0.62 eV to -1.12 eV due to preferable adsorption between Cu and TiC where charge polarization exists.<sup>52</sup> Therefore, our results show CO<sub>2</sub> adsorption on RuMo bimetallic phosphide becomes much more favorable than monometallic phosphides and thus, significantly activate CO<sub>2</sub> molecule for hydrogenation.

The correlation between CO<sub>2</sub> adsorption energy and CO normalized methanol formation rate is depicted in Fig. 5 (a). An overall trend was observed between CO<sub>2</sub> adsorption energy and methanol productivity for most of the catalysts, except for Ru<sub>0.8</sub>Mo<sub>1.2</sub>P, suggesting a higher overall reactivity can be correlated to a stronger interaction between CO<sub>2</sub> and the metal phosphide surface sites. Ru<sub>0.8</sub>Mo<sub>1.2</sub>P has lower activity than what was expected from the trend. Such unexpected variation in the property of bimetallic phosphide has been reported <sup>44, 47, 93, 94</sup> and can be attributed to a Mo-rich coordination environment where Mo sites are more likely to be locally surrounded by another Mo rather than Ru. Charge transfer between Mo and Ru is reduced compared to Ru<sub>1</sub>Mo<sub>1</sub>P, and the material behaves more similarly to MoP. In order to confirm the apparent trend

obtained from DFT calculations, the calculations were correlated with CO<sub>2</sub> temperature programmed desorption (TPD) experiments. Figure S4 and Table 2 show the CO<sub>2</sub> TPD results from MoP, Ru<sub>1</sub>Mo<sub>1</sub>P, Ru<sub>1,2</sub>Mo<sub>0,8</sub>P and Ru<sub>0,8</sub>Mo<sub>1,2</sub>P. The desorption of CO<sub>2</sub> on MoP exhibits one peak centered at 137 °C, indicating weak adsorption of CO<sub>2</sub> under these conditions. For comparison, the observed desorption temperature is lower than  $Mo_2C^{95, 96}$  (>300°C), a catalyst that is more active for CO<sub>2</sub> reduction to methanol.<sup>56</sup> The Ru-Mo bimetallic phosphides interact with  $CO_2$  differently (Figure S4). For each of these materials, two desorption peaks were observed: a weaker desorption peak centered in the lower temperature region (120 - 150 °C) and a stronger desorption peak centered in the higher temperature region (230 - 250 °C). In order to quantify the number of  $CO_2$  adsorption sites, the desorption profile was fitted with two gaussian peaks, representing weak adsorption sites (50 - 200 °C) and strong adsorption sites (>200 °C) on Ru-Mo bimetallic phosphides. The temperature of the desorption peaks and the amount of sites in each region summarized in Table 2. The CO<sub>2</sub> desorption temperature of Ru-Mo bimetallic phosphides is similar to Cu/ZnO<sup>97</sup> and much lower than calcium oxide-based (CaO) sorbents that are able to strongly bind CO<sub>2</sub> to form CaCO<sub>3</sub> above 500 °C,98 suggesting binding of CO<sub>2</sub> on Ru modified samples is not strong enough to irreversibly bind to the sites. We correlated these experimental binding results with the methanol production rates and computational results (Figure 5 (b)) by plotting the number of strong  $CO_2$  adsorption sites (N<sub>SAS</sub>) versus the methanol formation rate. As shown in Figure 5 (b), the number of strong adsorption sites on Ru<sub>1</sub>Mo<sub>1</sub>P is more than all other materials, with MoP providing no strong adsorption sites. The number of strong CO2 adsorption sites follows a same trend as the CO<sub>2</sub> binding energy:  $Ru_1Mo_1P$  (7.1  $\mu$ mol/g) >  $Ru_{0.8}Mo_{1.2}P$  (5.0  $\mu$ mol/g) > Ru<sub>1.2</sub>Mo<sub>0.8</sub>P (4.2  $\mu$ mol/g) > MoP (0  $\mu$ mol/g). These results strongly correlate with the DFT results showcasing that incorporation of Ru promotes CO<sub>2</sub> adsorption. A similar trend was

also discovered in Cu/Ti carbide (TiC), where an enhanced adsorption of CO<sub>2</sub> was found to decrease the activation energy barrier of methanol synthesis.<sup>52</sup> Higher adsorption energy of CO<sub>2</sub> may lead to faster formation and activation of reaction intermediates. These effects were also proposed on other bimetallic catalysts, such as Cu/Ni alloys, where Ni coverage on Cu (100) is proportional to methanol yield from CO<sub>2</sub> hydrogenation. <sup>99, 100</sup> A theoretical study revealed that the Ni-Cu interface can be a favorable adsorption site for CO<sub>2</sub> because of its stronger adsorption to the carbonyl O.<sup>99</sup> The stronger binding favors C-O bond cleavage during CO<sub>2</sub> hydrogenation and prevents desorption of reaction intermediates (e.g. CO) from the surface so that subsequent hydrogenation steps can proceed towards methanol synthesis. As for the Ru-Mo bimetallic phosphide, a similar effect could also exist. Therefore, not only CO<sub>2</sub> adsorption, but also the hydrogenation steps of reaction intermediates to methanol could be promoted by this bimetallic effect, which is an ongoing research topic in our groups.



**Figure 4.** Binding configuration of CO<sub>2</sub> over various metal phosphides: (a)  $Ru_1Mo_1P$  (112) (b)  $Ru_{0.8}Mo_{1.2}P$  (112) (c)  $Ru_{1.2}Mo_{0.8}P$  (112) (d)  $Mo_3P$  (321) (e) MoP (001) with surface P removed(f)  $Ru_2P$  (112) (g) RuP (211).



**Figure 5.** Methanol formation rates plotted as a function of (a) the calculated binding energy of  $CO_2$  on the metal phosphides and (b) the number of strong  $CO_2$  adsorption sites (N<sub>SAS</sub>) determined from the high temperature desorption peak.

Catalyst	Center of simulated desorption peak in low temperature region (°C)	Center of simulated desorption peak in high temperature region (°C)	Weak desorption sites (µmol/g)	Strong desorption sties (µmol/g)	Total desorption quantity (µmol/g)
MoP	137	_	1.2	0	1.2
$Ru_{0.8}Mo_{1.2}P$	144	227	3.4	5.0	8.4
$Ru_1Mo_1P$	122	220	2.0	7.1	9.1
$Ru_{1.2}Mo_{0.8}P$	121	229	2.3	4.2	6.5

Table 2. CO<sub>2</sub> desorption quantity for various catalysts

#### 3.5 Methanol Synthesis from CO/CO<sub>2</sub>/Formic Acid (FA) Hydrogenation

We also performed multiple experiments involving formic acid, CO, or CO/CO<sub>2</sub> mixtures as the feed to determine the catalytic performance of the metal phosphides in the presence of potential reaction intermediates.<sup>101</sup> Formate has been reported as a reaction intermediate in CO<sub>2</sub> hydrogenation, and the formation of formate from chemisorbed CO<sub>2</sub> is reported as a slow step that limits the rate of methanol formation.<sup>5</sup> By using formic acid as the primary reactant, the production of methanol can be studied without the initial CO<sub>2</sub> adsorption/hydrogenation steps.<sup>57</sup> Formic acid (FA) hydrogenation was performed with Ru<sub>1</sub>Mo<sub>1</sub>P, Ru<sub>2</sub>P and MoP at 200 °C. The hydrogen pressure, total pressure and temperature were kept identical to the previous CO<sub>2</sub> hydrogenation experiments for direct comparison. The conversion of FA was 100%, 100%, and 85% for Ru<sub>1</sub>Mo<sub>1</sub>P, MoP, and Ru<sub>2</sub>P, respectively. A portion of the conversion is inevitably attributed to the self-decomposition of formic acid, due to the 48% conversion of formic acid observed in the blank experiment without any catalyst.<sup>57</sup> However, methanol and trace amount of methyl formate were observed in the liquid phase only in the presence of all of the studied catalysts (Fig. 6 (a)). In comparison to CO<sub>2</sub> hydrogenation with Ru<sub>1</sub>Mo<sub>1</sub>P and MoP, more methanol was produced from this experiment by adding small amount of formic acid and 3 MPa H<sub>2</sub> as feed at same reaction temperature (i.e., 200°C), as shown in Fig. 6 (c). Namely, 16 times and 5 times more methanol was produced by using 2.4 mmol formic acid as feed than 1 MPa CO<sub>2</sub> (~20 mmol) with MoP and Ru<sub>1</sub>Mo<sub>1</sub>P respectively. This suggests formate as possible reaction intermediates for methanol synthesis with the phosphide catalysts because it can be converted to methanol at a faster rate than  $CO_2$  (Fig. 6(c)). Note that a part of the methanol produced might also come from  $CO_2$  that was formed after decomposition of formic acid with or without assistance of catalyst. The trend of methanol production is  $Ru_1Mo_1P > MoP > Ru_2P$  in these experiments, as is shown in Fig. 6 (a).

Higher methanol production indicates synergistic effect between Ru and Mo can accelerate formate hydrogenation to methanol, similar to what was observed on bimetallic carbide. <sup>57</sup> For MoP and Ru<sub>1</sub>Mo<sub>1</sub>P, a higher methanol formation rate from formic acid hydrogenation than CO<sub>2</sub> hydrogenation was observed, which suggests the formate pathway to methanol is likely to occur. Considering the trend of methanol production rates (Ru<sub>1</sub>Mo<sub>1</sub>P > MoP > Ru<sub>2</sub>P) as is shown in Fig. 6 (a), the higher methanol production demonstrates the importance of the bimetallic Ru-Mo sites in formate hydrogenation, similar to what was observed on bimetallic carbides.<sup>57</sup>

CO was also utilized as feed instead of CO<sub>2</sub> in order to investigate CO as possible reaction intermediates for methanol synthesis at 200 °C. Blank experiments (1) in the absence of catalyst and (2) without  $CO/CO_2$  were carried out respectively and no methanol was detected in the solvent, proving that methanol only comes from CO/CO<sub>2</sub> hydrogenation. From the CO hydrogenation experiments, Ru<sub>2</sub>P and MoP were much less active than Ru<sub>1</sub>Mo<sub>1</sub>P (Fig. 6 (b)). The methanol formation rate over MoP and Ru<sub>1</sub>Mo<sub>1</sub>P are 0.0003 and 0.00076 s<sup>-1</sup>, respectively. In order to compare the rate difference of methanol formation from CO and CO<sub>2</sub>, we also performed CO/CO<sub>2</sub> experiment where the feed is a mixture of CO/CO<sub>2</sub> where R represents the ratio of CO<sub>2</sub> to CO in the feed. The methanol production rate decreases linearly as the R value increases from 0 to 100, showing methanol synthesis from CO hydrogenation is more favorable than CO<sub>2</sub> hydrogenation over both MoP and Ru<sub>1</sub>Mo<sub>1</sub>P (Fig. 6 (d)). However, similar CO/CO<sub>2</sub> experiment was also performed by Duyar et al.<sup>11</sup> in gas phase, showing the methanol synthesis from CO<sub>2</sub> hydrogenation is slightly higher than CO hydrogenation over MoP/K-SiO<sub>2</sub>. This difference can be explained by the promotion effect of potassium on CO<sub>2</sub> hydrogenation. Previous computation work showed surface potassium has stronger promotion effect on activation of CO<sub>2</sub> than CO on Cu/CuO.<sup>102, 103</sup> This distinct promotion effect of potassium might be one reason for the difference between

unsupported MoP and MoP/K-SiO<sub>2</sub>. In addition, comparison of both Ru<sub>1</sub>Mo<sub>1</sub>P and MoP in Fig. 6 (d) shows that methanol production rate of Ru<sub>1</sub>Mo<sub>1</sub>P is 2-3 times higher than MoP, regardless of the CO<sub>2</sub>/CO ratio. Therefore, the result suggests CO may serve as a possible reaction intermediate over MoP and Ru<sub>1</sub>Mo<sub>1</sub>P. More importantly, it shows the active sites on Ru<sub>1</sub>Mo<sub>1</sub>P were much more effective in conversion of CO into methanol than MoP. Calculations were performed on Ru<sub>2</sub>P (112), MoP (001) and Ru<sub>1</sub>Mo<sub>1</sub>P (112) facets to investigate the energetics of CO adsorption on the various surfaces. The results provided in Table S9 indicate CO binding on Ru<sub>1</sub>Mo<sub>1</sub>P (112) is more favorable than MoP (001) and Ru<sub>2</sub>P (112). Thus, the improvement in methanol production rates over Ru<sub>1</sub>Mo<sub>1</sub>P are possibly due to a stronger CO binding energy that stabilizes CO species and allows for facile hydrogenation to methanol.



**Figure 6.** Methanol formation from FA hydrogenation after 5 hours with  $Ru_2P$ , MoP and  $Ru_1Mo_1P$  at 200°C (a). Methanol formation rates after 5 hours from CO hydrogenation at 200°C (b). Ratio of methanol synthesized from reaction intermediates (FA and CO) to methanol synthesized from  $CO_2$  at 200°C (c). Methanol formation rates after 5 hours versus the input CO/CO<sub>2</sub> ratio with  $Ru_1Mo_1P$  and MoP (d). Conditions: 200°C, (CO+CO<sub>2</sub>)/H<sub>2</sub>/He=1/2/3, initial pressure 3.7 MPa.

#### 3.6 Analysis of Gas Phase Products

The gas phase products over the various catalysts was also compared with a feed mixture of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> (CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub>=10/30/1) at 6.8 MPa and 200 °C. In order to quantify gas phase products, 0.01 MPa of N<sub>2</sub> was added into the feed mixture as internal standard, and the products were calibrated using external calibration curves from gas chromatography. The carbon balance

was calculated based on the sum of all C-containing products and the residual gas phase  $CO_2$  remaining in the system. For all experiments, the carbon balance was > 90%.

The selectivities of the gas products (CO and CH<sub>4</sub>) are shown in Fig. 7. Methane was found to be the only gas phase product for Ru<sub>2</sub>P, indicating Ru sites in the phosphides may favor methanation possibly due to the strong binding of CO with the Ru-rich catalyst. However, the gas phase products from RuP were also evaluated, yet no methane or CO were detected. The CO<sub>2</sub> binding energy on RuP (-0.5 eV) was calculated as the lowest among all of the catalysts in this study, and therefore, the interaction with CO<sub>2</sub> may be too weak to activate CO<sub>2</sub> and form CO or methane. As for the Mo-containing phosphides (MoP and Mo<sub>3</sub>P), CO was the only gas phase product detected. This result is similar to a previous study by Duyar et al. who also observed CO as the major product from MoP/K-SiO<sub>2</sub> at 230 °C.<sup>11</sup> Mo<sub>3</sub>P also produced only CO as a gas phase product, but it had a lower CO yield than MoP.

As for the bimetallic phosphides (Fig. 7), both CO and methane were observed in the gas phase regardless of the Ru:Mo ratio. However, the same trend was found that methane is the major product for Ru-rich samples, while the Mo-rich bimetallic catalyst produces more CO than methane. These results, taken in consideration with the monometallic results, show that methanation is promoted by the presence of Ru. The Ru-rich surface can facilitate hydrogen adsorption and dissociation, resulting in faster hydrogenation of adsorbed CO<sub>2</sub> to methanol, CO and methane.



**Figure 7.** Selectivity to gas phase products by using both monometallic and bimetallic phosphides. (selectivity at 5h, condition: 200 °C, initial pressure 6.8 MPa,  $CO_2/H_2/N_2=10/30/1$ )

## 3.7 Recyclability

Lastly, the recyclability and stability of the methanol synthesis catalyst is crucial to its overall catalytic performance. During CO<sub>2</sub> hydrogenation, several products such as water, CO, and methane can be formed. Conventional catalysts, such as Cu-based materials, can deactivate quickly due to sintering of Cu nanoparticles in the presence of water.<sup>16, 104</sup> In a batch reactor system, the deactivation could be a more severe problem since water can accumulate in the liquid phase instead of being continuously removed in flow reactor system. Therefore, we tested the stability of Ru<sub>1</sub>Mo<sub>1</sub>P in the same batch reactor for 24 hours at 200 °C. After each cycle, the catalyst was recovered by filtering and washing with pure 1,4-dioxane. Then Ru<sub>1</sub>Mo<sub>1</sub>P was dried in vacuum over at room temperature overnight before next cycle. Fig. 8 shows the methanol formation rate of Ru<sub>1</sub>Mo<sub>1</sub>P at each cycle. It is clear that the methanol formation rate after 4 cycles (96 hours) is

very close to the activity of fresh sample. The moisture concentration in the liquid phase was also measured by coulometric titration after cooling to room temperature. After 24 hours reaction, the water concentration in the solvent was determined as 6303 ppm for first cycle. Such high amount of water was not only produced by methanol synthesis from CO<sub>2</sub>, but also a result of methanation, reverse water gas shift reaction and other possible side reactions.<sup>11</sup> Therefore, Ru<sub>1</sub>Mo<sub>1</sub>P was stable even in the presence of water. This stability observation is similar with CO<sub>2</sub> hydrogenation over MoP/K-SiO<sub>2</sub><sup>11</sup> and water doping experiment performed on bimetallic phosphide (i.e., FeMoP)<sup>29</sup> No hydrogen regeneration was needed to recover the methanol productivity.



**Figure 8.** Recyclability experiments of Ru<sub>1</sub>Mo<sub>1</sub>P. Conditions: 30 mg catalyst in each cycle, 4 ml of 1,4 dioxane, 200 °C, and 24 h reaction time.

# 4. Conclusion

In summary, the CO<sub>2</sub> hydrogenation performance of monometallic and Ru-Mo bimetallic phosphides was evaluated by comparing methanol productivity. The Ru-Mo bimetallic phosphides outperformed MoP and other monometallic phosphides for methanol synthesis from CO<sub>2</sub>. Through

XPS experiments and DFT calculations, we observed charge transfer between the metals and phosphorous that altered the electron distribution on Ru and Mo sites in the bimetallic phosphides. DFT calculations reveal that adsorption energy of  $CO_2$  on the bimetallic catalysts is higher than the monometallic phosphides, allowing the bimetallic catalysts to more easily activate  $CO_2$  for subsequent hydrogenation steps. The DFT results were corroborated by  $CO_2$  TPD experiments, which showed the bimetallic Ru-Mo phosphides contained additional strong CO2 adsorption sites that were not observed on MoP. Hydrogenation reactions of mixed  $CO/CO_2$  feeds or formic acid also showed enhanced conversion of these potential reaction intermediates to methanol with Ru<sub>1</sub>Mo<sub>1</sub>P compared to the monometallic phosphides. Lastly, we tested the stability of Ru<sub>1</sub>Mo<sub>1</sub>P by collecting the catalyst after reaction and dispersing it in fresh solvent for re-evaluation. After three consecutive cycles, the methanol production rate was consistent and no deactivation was observed after 96 hours reaction at 200 °C.

Overall, a promotional effect from the synergy between Ru and Mo results in (1) enhanced adsorption and activation of CO<sub>2</sub> and/or (2) faster hydrogenation of reaction intermediates to methanol. These results showcase the ability to tune metal phosphides for improved performance, and this approach is applicable to other industrially significant reactions. Metal phosphides can be synthesized from most transitional metals and offer an extensive materials discovery space to identify optimal compositions for selective hydrogenations. As observed here, Ru addition to MoP also produced CH<sub>4</sub>. New approaches to suppress the methanation pathway by including promoters or additives should be considered. Alternatively, metal combinations that exclude Ru (or other methanation catalysts) can be identified and evaluated. These concepts are part of ongoing research in our laboratory that can lead to the advancement of CO<sub>2</sub> conversion technologies.

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Notes

The authors declare no competing financial interest

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