Electronic Supplementary Information

Direct synthesis of Furfuryl Alcohol from Furfural: Catalytic Performance of Monometallic and Bimetallic Mo and Ru Phosphides

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Synthesis and characterization of monometallic and bimetallic Ru and Mo phosphides

MoP and Mo_3P

MoP was synthesized by mixing 1.1613 g of citric acid (CA) followed by 1.3247 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 1.0107 g of $(NH_4)_2HPO_4$ in 50 mL 18 mΩ water. The solution was left mixing for at least 1 h before it was dried to 25 mL using rotary evaporator. The thick solution was calcined at 200°C for 2 hr with ramp rate of 1°C/min using Lindberg Blue M calcination oven. The resulting cake was grinded and calcined further at 550°C for 4.5 h with ramp rate 1°C/min. Lindberg Blue M mini-mite tube furnace was used to reduce the powder under 160 mL/min of H_2 flow at 650°C for 2 h using ramp rate of 5°C/min. The phosphides were passivated for 1 h under 160 mL/min of 1% O_2/He before it was stored in the N_2 glove box.

Mo_3P was synthesized in a similar manner starting with 1.7420 g of CA, 1.9870 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.4952 g of $(NH_4)_2HPO_4$ in 50 mL 18 mΩ water. The reduction temperature of the post-calcination Mo_3P was 800°C.

The formation of MoP and Mo_3P crystal structures were confirmed using Bruker powder x-ray diffraction (XRD) with Cu Kα source. The diffraction pattern of MoP was shown in Figure S1A.a. Three of the most dominant peaks (101), (100), and (110) respectively was matched with its reference pattern in Figure S1A.b. Similarly, the three most dominant peaks in Mo_3P (321), (411), and (112) was matched between the sample diffraction (Figure S1A.c) and the reference pattern (S1A.d). Based on the XRD results, both MoP (hexagonal) and Mo_3P (tetragonal) were successfully synthesized. The diffraction pattern of $Ru_xMo_{2-x}P$ was discussed in the main manuscript. The ratio used to denote the material composition was based on ICP-OES result.

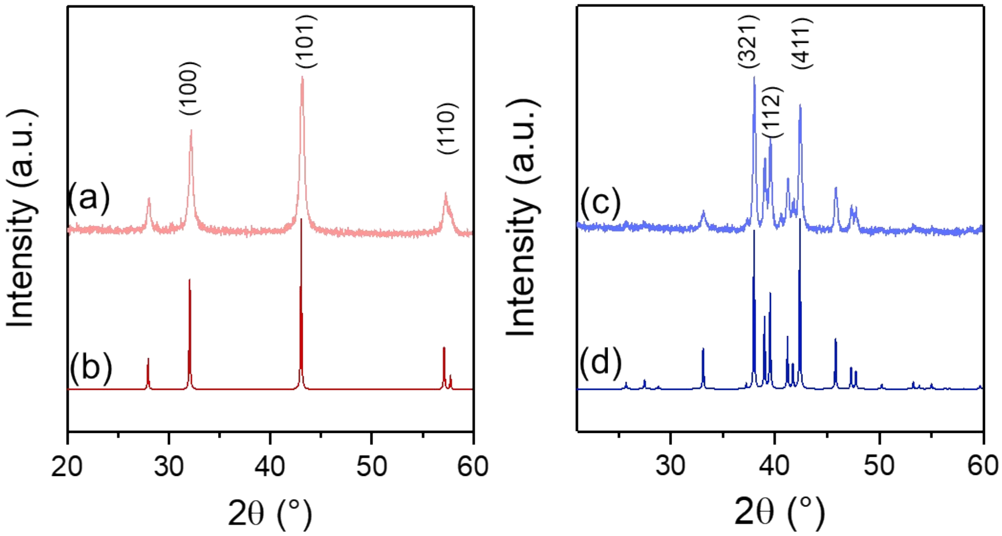

Figure S1. XRD patterns of (a) MoP (b) MoP reference (PDF 04-002-4743) (c) Mo_3P (d) Mo_3P reference (PDF 03-065-1609)

RuP and Ru_2P

RuP and Ru_2P were synthesized in a similar manner as the Mo phosphides. The following recipes are used to make the initial solution:

- RuP: 1.1613 g of CA, 2.1267 g of $RuCl_3\cdot xH_2O$ and 1.0107 g of $(NH_4)_2HPO_4$ in 50 mL 18mΩ water
- Ru_2P, 1.5484 g of CA, 2.8357 g of $RuCl_3\cdot xH_2O$, and 0.6738 g of $(NH_4)_2HPO_4$ in 50 mL 18mΩ water

The diffraction pattern was confirmed with powder XRD. RuP (Figure S1B.a) adapted the orthorhombic crystal structure with (011), (211), and (112) being the most dominant facets. These facets matched the reference pattern from RuP (Figure S1B.b). Ru_2P (Figure S1B.c) also adapted the orthorhombic crystal structure with (211), (121), and (002) as the most dominant facets respectively. They were matched to Ru_2P reference pattern (Figure S1B.d). The diffraction pattern of $Ru_xMo_{2-x}P$ was discussed in the main manuscript. The ratio used to denote the material composition was based on ICP-OES result.

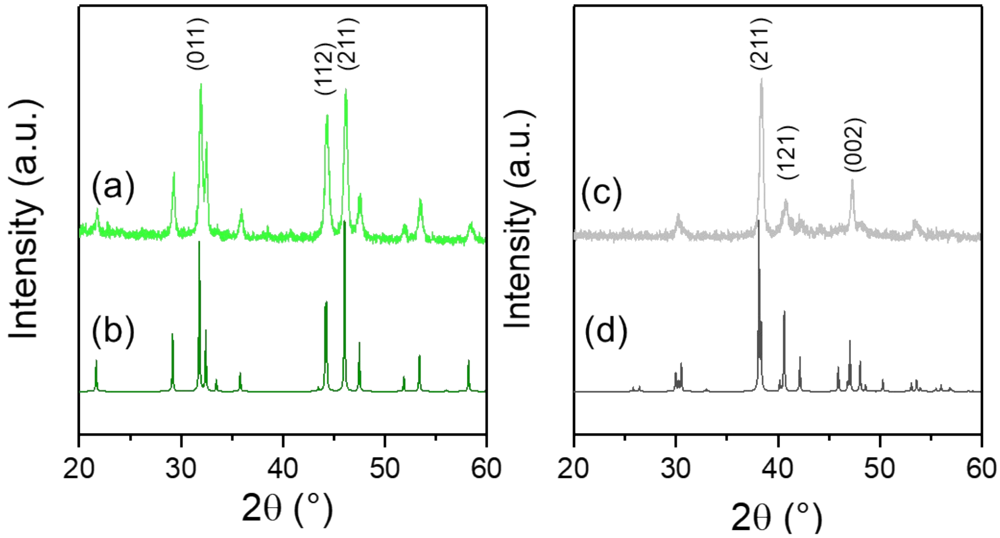

Figure S2. XRD patterns of (a) RuP (b) RuP reference (PDF 04-004-3077) (c) Ru_2P (d) Ru_2P reference (PDF 04-004-4140)

$Ru_xMo_{2-x}P$

Bimetallic $Ru_xMo_{2-x}P$ was synthesized using the same method as the monometallic phosphides. The following recipes are used to make the initial solutions:

- $Ru_{0.8}Mo_{1.2}P$: 1.5484 g of CA , 1.0597 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 1.1343 g of $RuCl_3\cdot xH_2O$, and 0.6738 g of $(NH_4)_2HPO_4$ in 50 mL 18mΩ water
- $Ru_{1.0}Mo_{1.0}P$: 1.5484 g of CA, 0.8831 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 1.4178 g of $RuCl_3\cdot xH_2O$, and 0.6738 g of $(NH_4)_2HPO_4$ in 50 mL 18mΩ water

- $Ru_{1.2}Mo_{0.8}P$: 1.5484 g of CA, 0.7065 g of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, 1.4178 g of $RuCl_3\cdot xH_2O$, and 0.6738 g of $(NH_4)_2HPO_4$ in 50 mL 18mΩ water

The diffraction pattern of $Ru_xMo_{2-x}P$ was discussed in the main manuscript. The ratio used to denote the material composition was based on ICP-OES result.

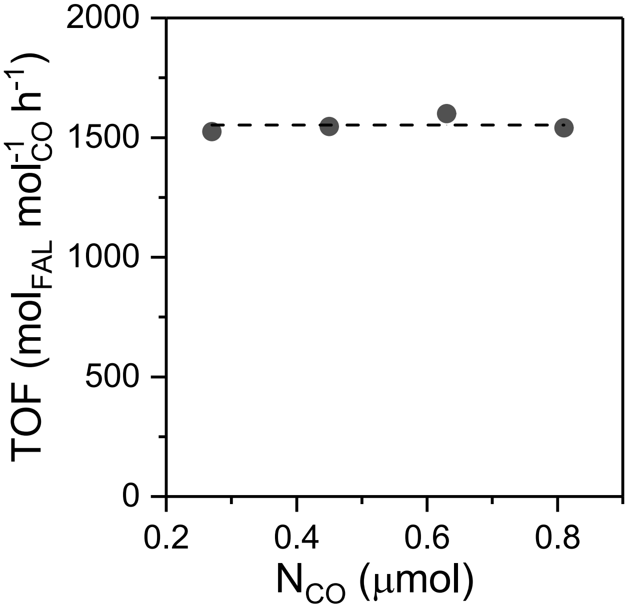

Figure S3. TOF correlation with the increase in amount of catalyst used in the experiments. The difference between each point are < 5%.

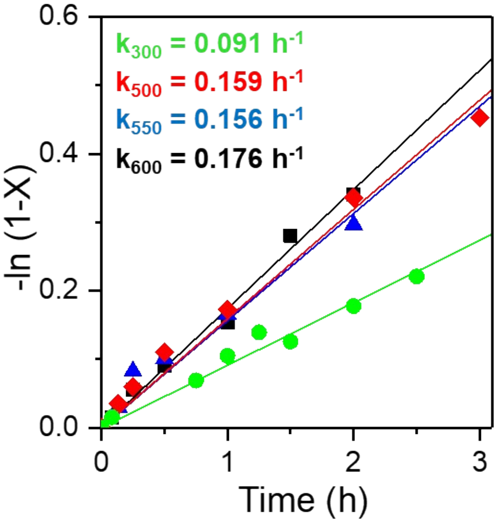

Figure S4. H_2 dependency for FAL hydrogenation with $Ru_{1.0}Mo_{1.0}P$ reaction performed at 2.0 MPa (green – $R^2 = 0.973$), 3.4 MPa (red – $R^2 = 0.983$), 3.8 MPa (blue – $R^2 = 0.946$), and 4.2 MPa (black – $R^2 = 0.981$) H_2 partial pressure and total pressure of 4.2 MPa at 100°C and 0.10 M FAL in IPA

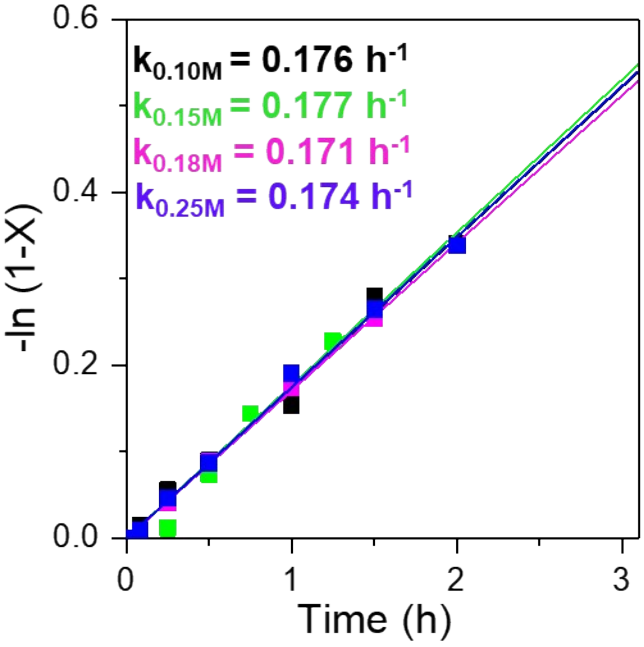

Figure S5. First order dependency of FAL concentration measured for initial concentration of 0.10 M (black – $R^2 = 0.981$), 0.15 M (green – $R^2 = 0.975$), 0.18 M (magenta – $R^2 = 0.978$), and 0.25 M (blue – $R^2 = 0.986$)

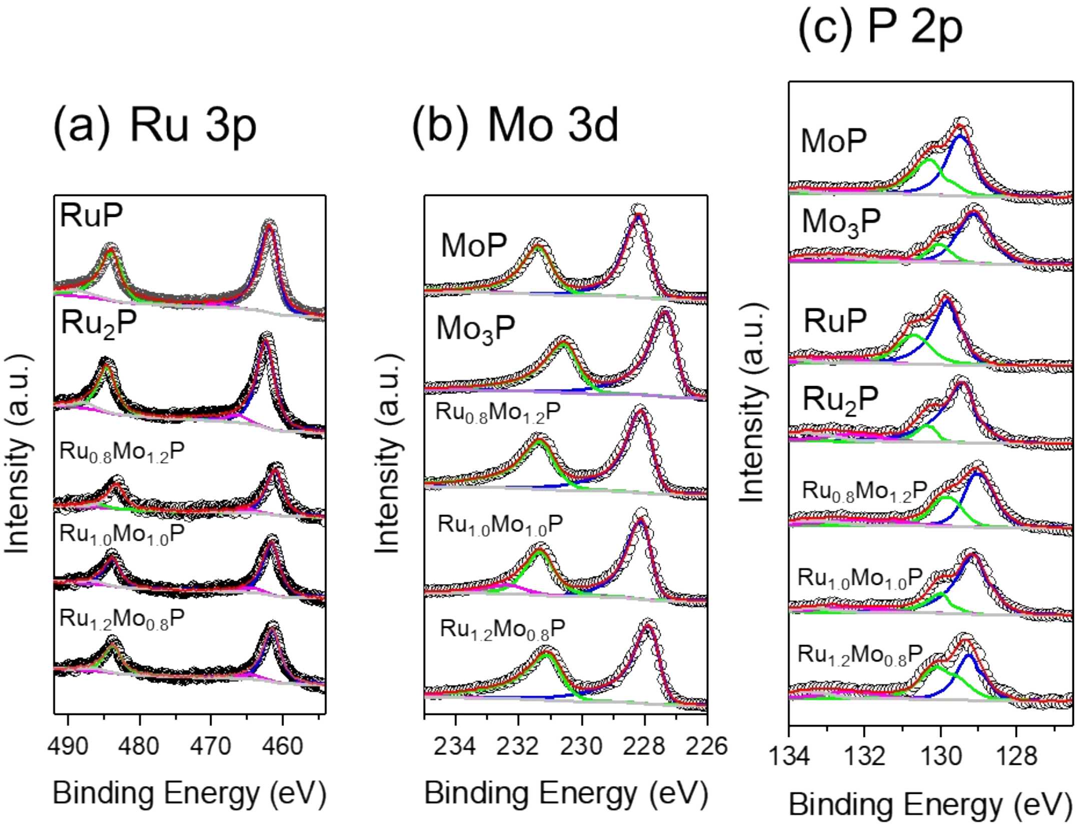

Figure S6. XP spectra deconvolution for (a) reduced Ru $3p_{3/2}$ (blue), reduced Ru $3p_{1/2}$ (green), oxidized Ru $3p_{3/2}$ (magenta), oxidized Ru $3p_{1/2}$ (gray), (b) reduced Mo $3d_{5/2}$ (blue), reduced Mo $3d_{3/2}$ (green), oxidized Mo $3d_{5/2}$ (magenta), oxidized Mo $3d_{3/2}$ (gray), and (c) reduced P $2p_{3/2}$ (blue), reduced P $2p_{1/2}$ (green), oxidized P $2p_{3/2}$ (magenta), oxidized P $2p_{3/2}$ (gray). The raw spectrum is represented by the empty circles and the fit is represented by the red line.

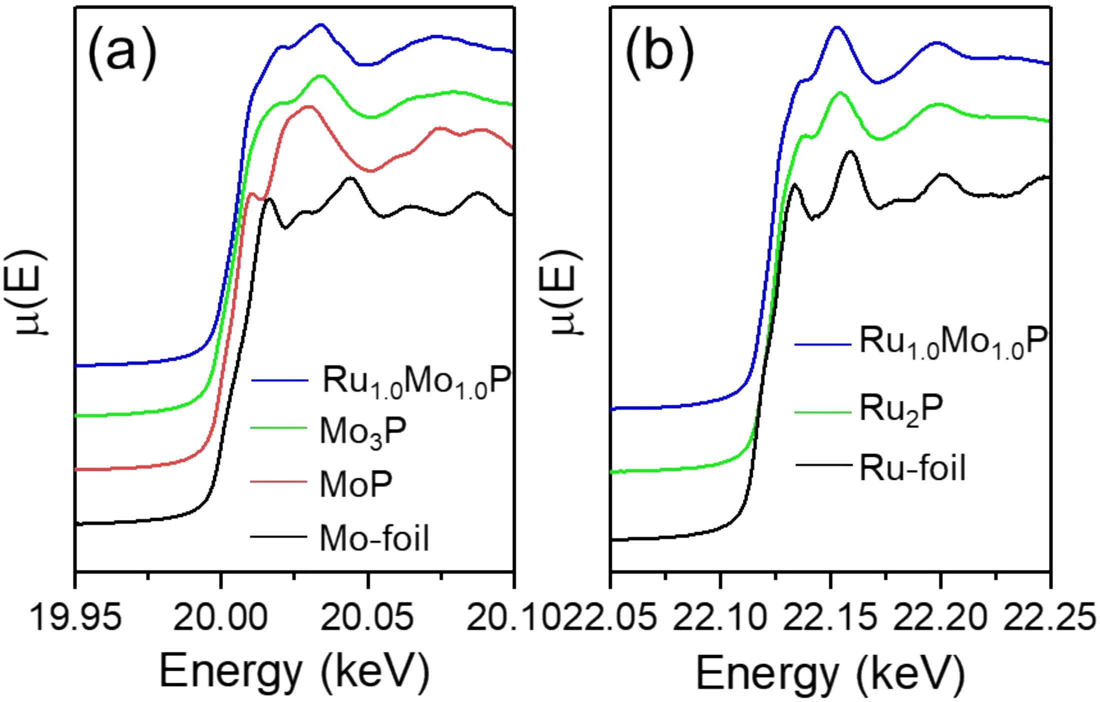

Figure S7. (a) Mo K-edge XANE spectra of Mo-foil (black), MoP (red), Mo_3P (green), $Ru_{1.0}Mo_{1.0}P$ (blue) and (b) Ru K-edge XANE spectra of Ru-foil (black), Ru_2P (green), $Ru_{1.0}Mo_{1.0}P$ (blue).

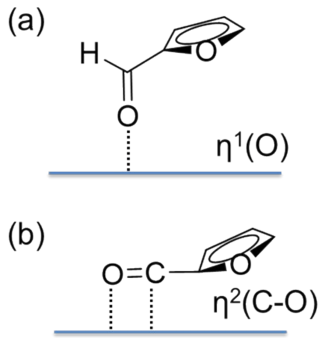

Figure S8. Two possible adsorption modes on the catalyst surface: (a) η^1(O) was observed on Cu, (b) η^2(C-O) suggested on group VIII metals

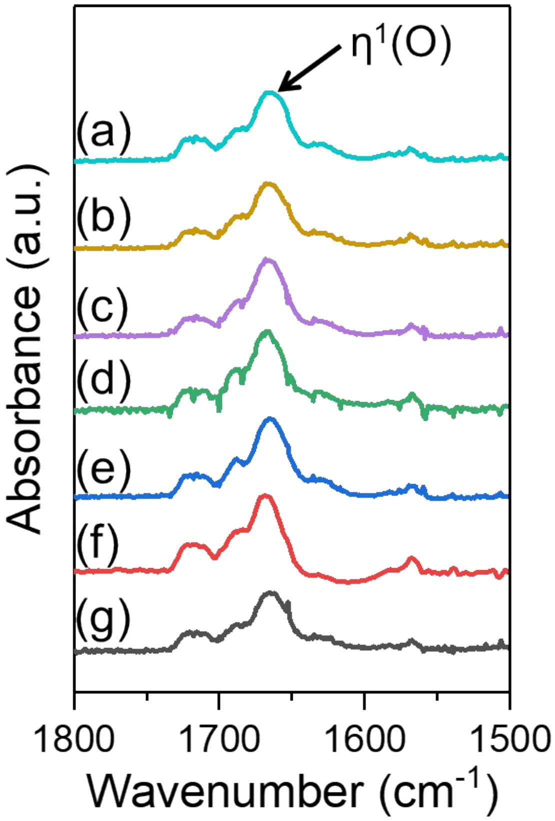

Figure S9. DRIFT spectra of FAL on (a) Cu/SiO_2 (b) MoP (c) Ru_2P (d) RuP (e) $Ru_{0.8}Mo_{1.2}P$ (f) $Ru_{1.0}Mo_{1.0}P$ (g) $Ru_{0.8}Mo_{1.2}P$.

Table S1. Cell parameters for $Ru_xMo_{2-x}P$ calculated from Rietveld refinement (experimental) and computationally using 1 X 4 X 2 supercell via optB88-vdW functional.

cell parameter (Å)	$Ru_{1.2}Mo_{0.8}P$		$Ru_{1.0}Mo_{1.0}P$		$Ru_{0.8}Mo_{1.2}P$	
	Exp.	Comp.	Exp.	Comp.	Exp.	Comp.
b	13.46	13.32	15.41	15.45	15.65	15.58
c	13.72	13.68	13.88	13.85	14.23	14.25

Table S2. Summary of material composition determined with ICP-OES and XPS normalized to the amount of P

Entry	Material	ICP-OES			XPS		
		Ru	Mo	P	Ru 3*p*	Mo 3*d*	P 2*p*
1	MoP		1.0	1.0	-	1.1	1.0
2	Mo_3P		3.0	1.0	-	2.9	1.0
3	RuP	1.0		1.0	1.0	-	1.0
4	Ru_2P	1.9		1.0	1.8	-	1.0
5	$Ru_{0.8}Mo_{1.2}P$	0.8	1.2	1.0	0.7	1.3	1.0
6	$Ru_{1.0}Mo_{1.0}P$	1.0	1.0	1.0	1.0	1.0	1.0
7	$Ru_{1.2}Mo_{0.8}P$	1.2	0.8	1.0	1.2	0.7	1.0

Table S3. Reaction rate constant values for all catalysts

	k_1 (h^{-1})	k_2 (h^{-1})	k_3 (h^{-1})	R^2, k_2 vs. k_3
MoP	0.029	0.0035		
RuP	0.030	0.0013	0.0185	0.922
Ru_2P	0.027	0.0002	0.1752	0.949
$Ru_{0.8}Mo_{1.2}P$	0.078	0.0106		
$Ru_{1.0}Mo_{1.0}P$	0.176	0.0050	0.0039	0.977
$Ru_{1.2}Mo_{0.8}P$	0.258	0.0035	0.0134	0.971

Table S4. XPS binding energy shift and XANES adsorption energy of monometallic Mo phosphides and Ru phosphides

Material	Binding energy (eV)			Adsorption energy (eV)	
	Ru $3p_{3/2}$	Mo $3d_{5/2}$	P $2p_{3/2}$	Ru K-edge	Mo K-edge
MoP	-	228.2	129.5	-	20,001.25
Mo_3P	-	227.5	129.1	-	20,000.61
RuP	461.8	-	129.6	-	-
Ru_2P	462.0	-	129.4	22,117.42	-

Table S5. Bader charge calculations on (112) and (210) facet of $Ru_{1.0}Mo_{1.0}P$

Atom	Bader charges (eV)	
	(112) facet	(210) facet
Ru	-0.23	-0.25
Mo	+0.70	+0.71
P	-0.46	-0.46

Table S6. Surface and bulk Bader charges of monometallic and bimetallic phosphides. The surface charges are calculated as the sum of Bader charges of one atom on the top-most layer. The bulk charges are the sum of Bader charges present in the total layers of catalytic system or supercell.

Material	Surface charges ($\lvert e \rvert$)			Bulk charges ($\lvert e \rvert$)		
	Ru	Mo	P	Ru	Mo	P
MoP	-	+0.52	-0.52	-	+0.52	-0.52
Mo_3P	-	+0.91	-0.91	-	+0.30	-0.91
RuP	+0.11	-	-0.11	+0.11	-	-0.11
Ru_2P	+0.13	-	-0.13	+0.06	-	-0.13

Table S7. Perpendicular distance (d, Å) of carbon and oxygen atoms of carbonyl group of trans-furfural and center of mass (COM) of furanic ring from the surface after horizontal adsorption on (112) facet of $Ru_{0.8}Mo_{1.2}P$, RuMoP, and $Ru_{1.2}Mo_{0.8}P$ catalysts.

Atom	$Ru_{0.8}Mo_{1.2}P$	$Ru_{1.0}Mo_{1.0}P$	$Ru_{1.2}Mo_{0.8}P$
C	1.35	1.31	2.22
O	1.71	1.51	2.33
COM	1.73	1.68	3.51

Dixon q-test

$$Q_{0.176} = \frac{gap}{range} = \frac{|0.176 - 0.159|}{|0.176 - 0.156|} = 0.85 \qquad \text{(Equation S1)}$$

At 90% confidence level, the $Q_{0.176}$ (0.85) is less than the rejection Q (0.94). Therefore, the data point can be identified as similar.