Supplemental Document

The P_x-Ru(0001) surfaces (x is the coverage of P-atoms in monolayer equivalents) are prepared by dosing PH_3 gas onto Ru(0001) at 298 K, followed by a 1300 K flash anneal. The composition and structure of the resulting surfaces are characterized by Auger electron spectroscopy (Figure 1) and low-energy electron diffraction (Figure 1 inset).[1,2]

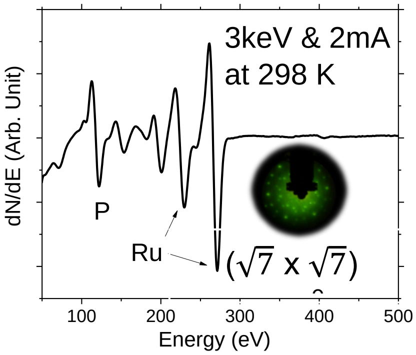

Figure 1: Auger electron spectra acquired on $P_{0.4}$-Ru(0001) at 298 K, with a low energy electron diffraction pattern of √7x√7 pattern (inset).

P_x-Ru(0001) surfaces are chemically characterized using CO (Figure 2) and NH_3 temperature programmed desorption (TPD). TPD results demonstrate that the addition of P atoms to Ru(0001) decreases the binding energy of CO by 12 ± 2 kJ mol^{-1} at $\theta < 0.33$ ML and that of NH_3 by 11 ± 2 kJ mol^{-1} at $\theta < 0.1$ ML compared with Ru(0001).

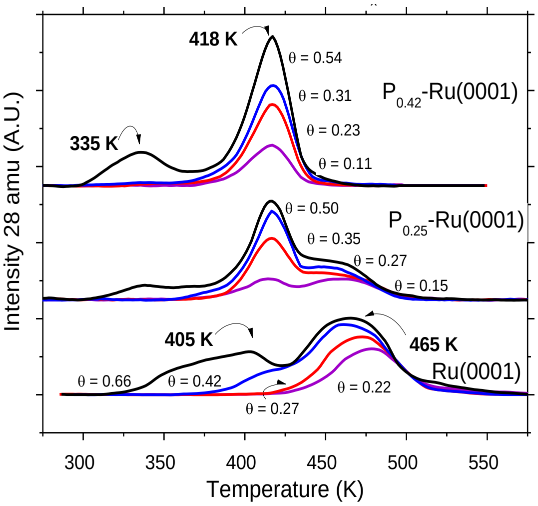

Figure 2: Temperature programmed desorption spectra of CO from Ru(0001), $P_{0.25}$-Ru(0001), and $P_{0.42}$-Ru(0001). CO was adsorbed at 95 K and heated to 800 K at 3 K s^{-1}.

The TPR results of C_1-C_4 carboxylic acid (e.g., formic acid (FA), acetic acid (AA), propionic acid (PA), and butyric acid (BA)) CO_2 production shown in Figure 3, illustrate that the addition of P atoms to Ru(0001) increases E_a values for the rupture of C-H and C-C bonds, by 5-50 kJ mol^{-1} (E_a values are determined using inversion analysis of the TPR results).[2] In addition, the integrated peak area of CO to CO_2 production also increases with the addition of P atoms (Figure 4).[3]

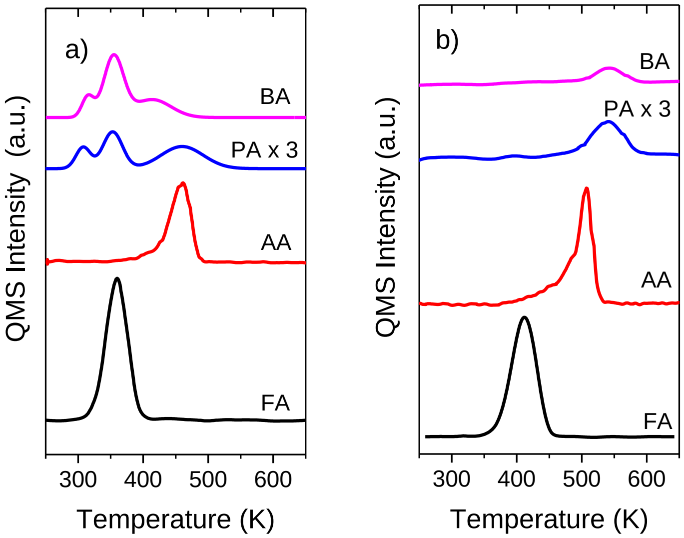

Figure 3: Production of CO_2 on a) Ru(0001) and b) $P_{0.4}$-Ru(0001) from temperature programmed reaction of formic acid (black), acetic acid (red), propionic acid (blue), and butyric acid (pink) at saturation dosage at 250 K and heated at a rate of 3 K s^{-1}.

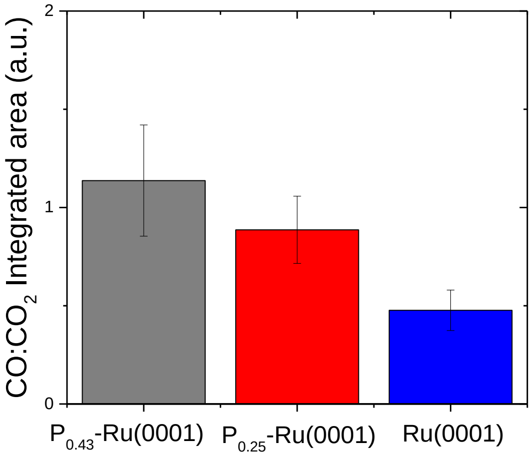

Figure 4. Integrated intensity of CO to CO_2 obtained from TPR of formic acid (DCOOH) over Ru(0001), $P_{0.25}$-Ru(0001), and $P_{0.42}$-Ru(0001). Uncertainties were determined from the standard deviation of four repeated experiments.[1]

References

1 S. A. Chang and D. W. Flaherty, J. Catal (in review) (2017).
2 S. A. Chang and D. W. Flaherty, J Phys Chem C **120** (44), 25425-25435 (2016).
3 S. A. Chang and D. W. Flaherty, J. Vac. Sci. Technol., A (in review) (2017)