Supporting Information for

Influence of Steam on a Vanadyl Pyrophosphate

Catalyst During Propane Oxidation

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X-ray powder diffraction of VPP

The X-ray powder diffraction (XRPD) measurements were performed in Bragg-Brentano geometry on a Bruker AXS D8 Advance II theta/theta diffractometer with Ni filtered Cu Kα radiation. A position sensitive energy dispersive LynxEye silicon strip detector was used. Figure S1 shows the XRPD pattern before and after the operando microwave conductivity experiment.
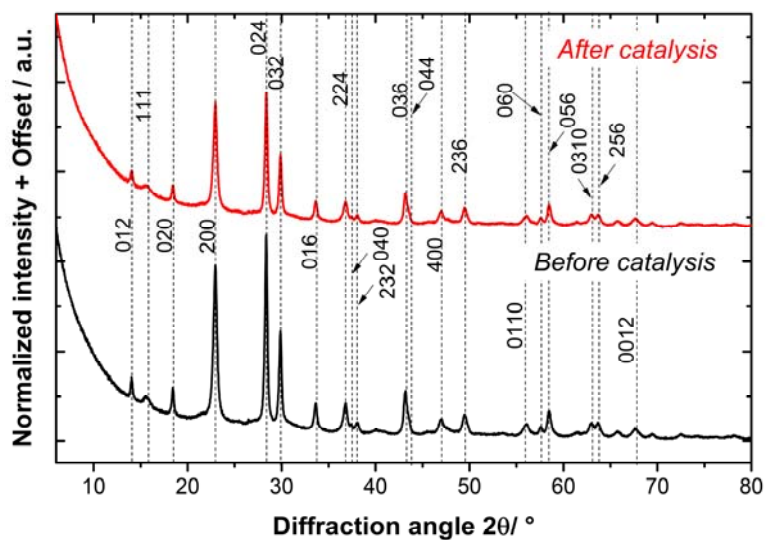

Figure S1. XRPD pattern of polycrystalline VPP before and after use in propane oxidation at 400 °C under the various feed compositions specified in the main text.
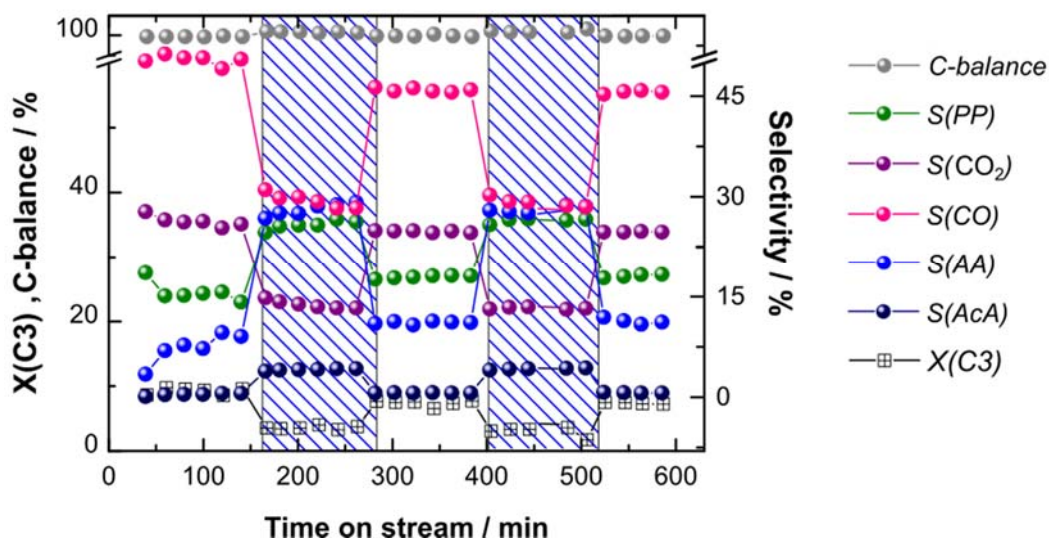
Operando microwave conductivity of VPP

Figure S2. Catalytic performance under dry (3 vol% C3, 6 vol% O_2, inert) and wet (3 vol% C3, 6 vol% O_2, 5 vol% steam, inert) feed conditions at 400 °C measured in the MCPT setup; X describes the conversion of propane; S describes the selectivity to propylene (PP), acrylic acid (AA), acetic acid (AcA), CO and CO_2. The hatched sections stand for wet conditions.
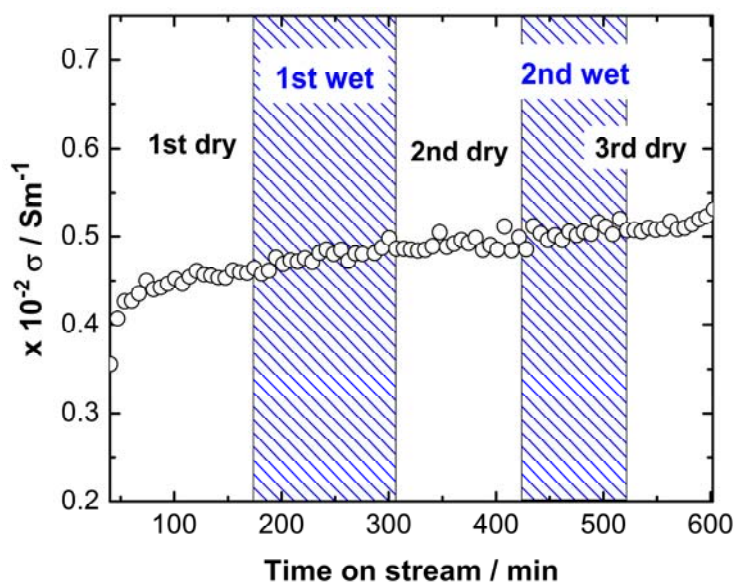

Figure S3. Microwave conductivity σ of VPP under dry (6 vol% O_2, inert) and wet (6 vol% O_2, 5 vol% steam, inert) feed conditions at 400 °C.

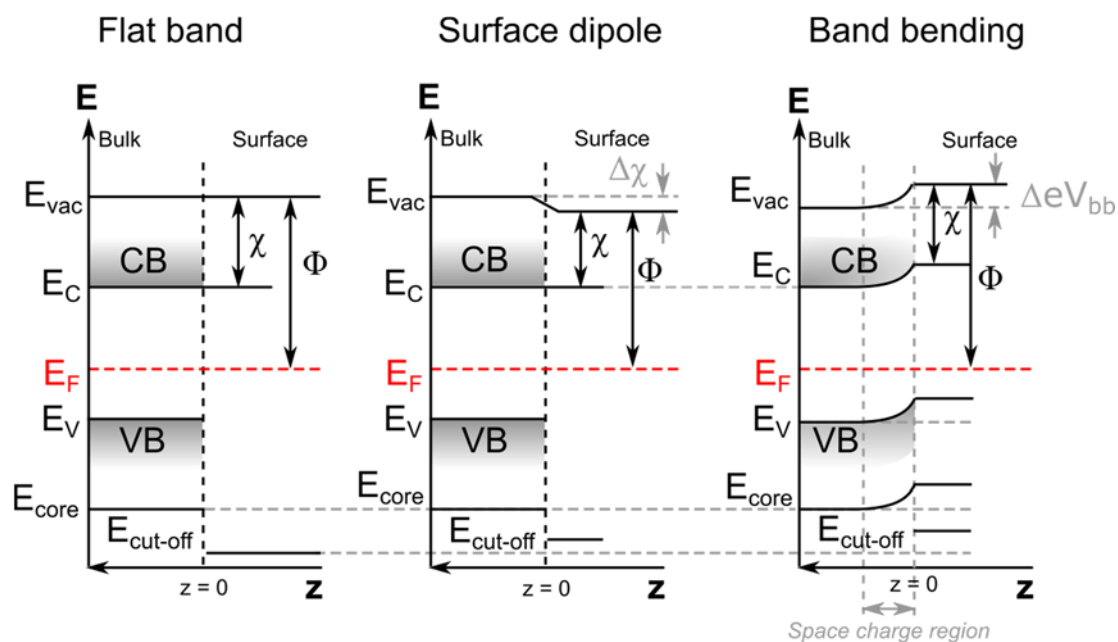# Near-ambient pressure X-ray photoelectron spectroscopy

Figure S4. Schematic changes of energetic conditions at a p-type semiconductor interface for flat band, surface dipole, and band bending situations. Further, E_{vac} is the vacuum level, E_C is the conduction band (CB) edge, E_F is the Fermi level, E_V is the valence band (VB) edge, E_{core} is the core level, $E_{cut-off}$ is the secondary electron cutoff edge, χ is the electron affinity, and Φ is the work function. The changes of surface dipole modification shifts $\Delta\chi$. The term eV_{bb} considers band bending.[1]

Table S1. V2p$_{3/2}$ fit parameters (see Figure 4 in in the main article) where FWHM is the full width at half maximum and GL is the Gaussian-Lorentzian ratio as defined in CasaXPS[2]

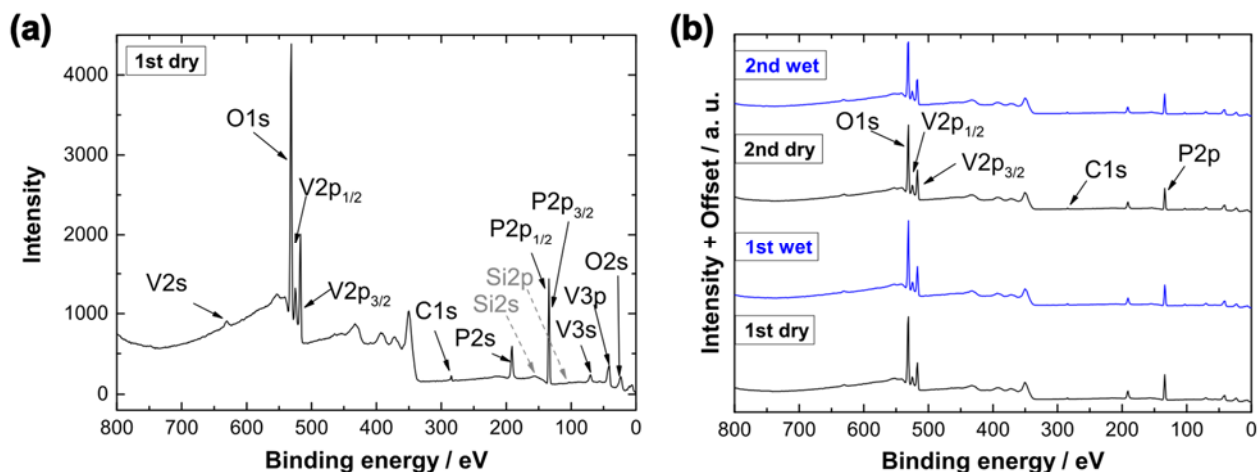| Species	V2p$_{3/2}$ V^{4+}	V2p$_{3/2}$ V^{5+} (I)	V2p$_{3/2}$ V^{5+} (II)
FWHM	1.72 - 1.66	1.58 – 1.61	1.58 – 1.61
Peak position / eV	516.9	518.0	517.8
Line shape	GL(45)	GL(45)	GL(45)

Figure S5. The XPS core level peak assignment of the survey spectra of VPP for the 1st dry feed **(a)**, and XP survey spectra (E_{ph} of 860 eV) of VPP for all applied gas feeds **(b)**.
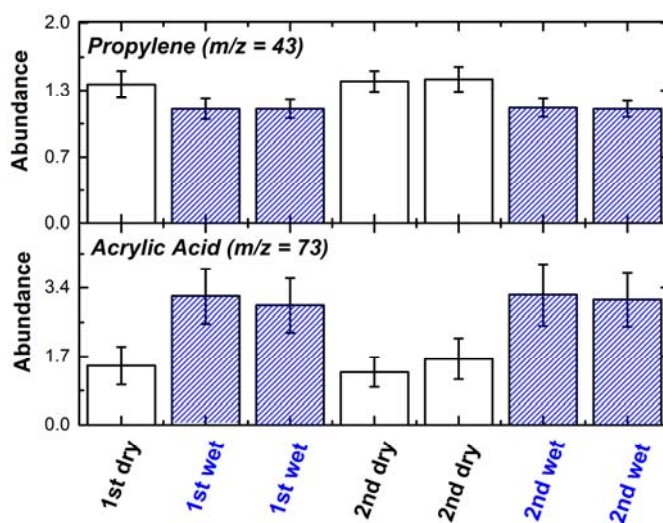

Figure S6. PTR-MS trace of propylene (top, protonated mass m/z = 43) and acrylic acid (bottom, protonated mass m/z = 73) under the various feed compositions as indicated on the abscissa.

References

(1) Aruchamy, A., *Photoelectrochemistry and Photovoltaics of Layered Semiconductors.* Springer Science & Business Media: 2013; Vol. 14.
(2) Schwab, G. M., Boundary-Layer Catalysis. *Angewandte Chemie International Edition in English* **1967,** *6*, 375-375.