Text S3. Operando ATR-FTIR characterization.

The electrochemical in situ attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Bruker Tensor II. A customized three-electrode spectroelectrochemical cell with a single semicylindrical silicon crystal was applied to conduct in situ ATR-FTIR measurements. Before experiments, a thin layer of gold (Au) film was chemically deposited on the smooth surface of a silicon crystal. The catalysis was carefully peeled off from the monolithic electrode and then mixed with Nafion solution to form a homogenous slurry. A 100 μL sample slurry was uniformly dropped on the surface of the gold film, which was taken as the working electrode. Meanwhile, a saturated calomel electrode and a Pt wire served as reference and counter electrode, respectively. The LSV tests were carried out with a scan rate of 2 mV/s and applied potentials ranging from 0.3 to −0.7 V vs. RHE. Corresponding ATR-FTIR spectra were continuously scanned 32 times with a resolution of 4 cm^{-1} and a time interval of 30 s.