

Supporting Information

Spectroscopic investigation of the electrosynthesis of diphenyl carbonate from CO and phenol on gold electrodes

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1. Experimental details:

The experiments were performed using a spectroelectrochemical cell with a three electrode configuration as described elsewhere^{8,9}. An Au disc was used as working electrode. Before each experiment the Au disc was mechanically polished with alumina suspension, rinsed with MilliQ water (18.4 MΩ.cm), sonicated for 5 min and finally flame annealed. A Pt coil was used as counter electrode and an Ag/AgCl electrode as reference. The electrode potential was controlled with a Potentiostat 466 System (Model ER466) from E-DAQ. All the experiments were performed at room temperature.

The electrolyte solution was prepared with 0.1 M LiClO₄ (Fluka, <99%) in methanol (MeOH, 98% anhydrous from Sigma Aldrich) to which phenol (PhOH, ACS reagent, ≥99.0% from Sigma) was added when appropriate. Some experiments were performed in a different solvent, acetonitrile 98% anhydrous from Sigma Aldrich (MeCN). Prior to the experiments the solutions were purged with Ar

(6.0 from Linde) to remove all the oxygen, and blank spectra were obtained. For the experiments with CO, the solutions was purged with CO (6.0 Linde) during 20 min after oxygen removal. During the spectroelectrochemical measurements, the gas flow was kept in the cell atmosphere.

For the in situ Fourier Transform Infra-Red (FTIR) Spectroscopy experiments, a Bruker Vertex 80 V IR spectrophotometer was used. The experiments were performed in external configuration using a CaF_2 prism bevelled at 60° and the electrode was pressed against the prismatic window at a controlled potential in a thin layer configuration (Figure S1) . The presented spectra correspond to an average of 100 interferograms with 8 cm^{-1} resolution and *p*-polarized light. The spectra in this work are presented as absorbance, according to $A = -\log(R/R_0)$ where R and R_0 are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively. As a consequence, positive bands correspond to species which concentration increases from reference to the sample potential and negative bands to species that decrease in concentrations from reference to sample potential.

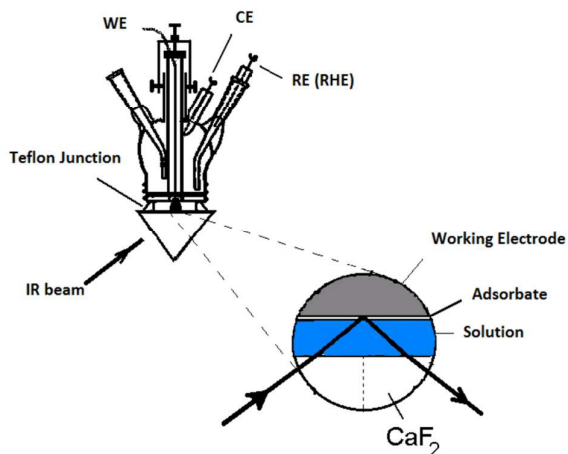


Figure S1: Scheme of the spectroelectrochemical cell used in this work.

2. Transmission spectra of 0.1 M PhOH in 0.1M LiClO_4 in MeOH

The transmission spectrum for PhOH in a MeOH solution presents 4 vibrational features at 1598, 1505, 1473, 1358 cm^{-1} . See Figure S2.

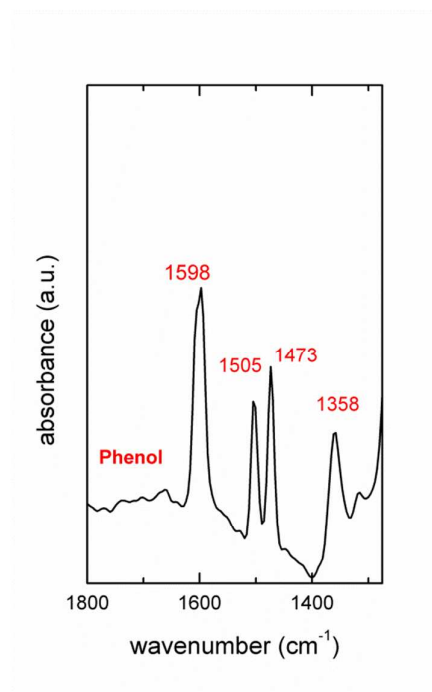


Figure S2: Transmission spectra of 0.1 M PhOH in 0.1M LiClO₄ in MeOH