

# The Role of Pyridine in the Electrochemical Reduction of CO<sub>2</sub>

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## Abstract:

Rising carbon dioxide (CO<sub>2</sub>) emissions are a major factor in the rise of the global temperature leading to issues associated with climate change. Capturing and converting CO<sub>2</sub> to useful chemicals that can be used for energy or industrial needs can help allay global warming whilst creating new, sustainable economic development. Electrochemical reactions (ECRs) with platinum (Pt) electrodes have been extensively studied for CO<sub>2</sub> reduction and have shown to heavily favor the hydrogen reduction reaction (HER). There has been a dispute as to whether the addition of pyridine enhanced the production of organic compounds such as methanol and formic acid. Through the *in-situ* use of Sum Frequency Generation spectroscopy (SFGs), a surface sensitive technique, during the ECR of CO<sub>2</sub>, we have shown that intermediates and products for organic product formation do not appear at the reaction interface. It also shows that pyridine most likely lays flat on the catalytic surface possibly blocking CO<sub>2</sub> adsorption sites.

## Summary of Research:

CO<sub>2</sub> adsorbed on the Pt surface as CO<sub>ads</sub> has been a known poison hindering its electrochemical reduction to organic products [1]. The addition of pyridine to this system was thought to enhance organic product formation [2] even though conflicting studies have shown the hydrogen reduction reaction (HER) was favored [3]. The question remained as to what chemical species were present at the catalytic interface.

Sum Frequency Generation spectroscopy (SFGs) was used as a tool for *in-situ* investigation of the species at the interface. SFG is powerful in that it only detects species at a non-centrosymmetric interface via the use of two spatially and temporally overlapped lasers. There are no contributions from any species in bulk solution to the detected signal. The electrochemical cell used for the *in-situ* study was filled with 0.1M NaClO<sub>4</sub> solutions. This solution either contained 0.01M pyridine or it did not, and both were in the presence of CO<sub>2</sub>. The working electrode was a Pt disk, the counter-electrode was Pt, the reference electrode was Ag/AgCl (NaCl saturated), the optical window used was made of CaF<sub>2</sub>, and the SFG

was measured in the ppp polarization combination. Complimentary cyclic voltametric (CV) studies were done for each system.

SFG was conducted first on the solution that had no pyridine with the electrode saturated with CO<sub>ads</sub>. Figure 1 shows that as the overpotential is lowered from -400mV to -1000mV there is a red shift of the CO<sub>L</sub> peaks, which is as expected from previous works [4-6]. The peaks were fit to a Lorentzian lineshape to elucidate the characteristic spectral features. The resulting Stark shift from this system (from the decreasing peak center with potential) was higher than reported number most likely due to a differing cationic structure at the interface in the presence of the applied field. The frequency shift is also characteristic of either dipole-dipole coupling or an increase in the back-donation of electrons from the Pt surface to the CO π\* antibonding orbitals [7]. A decrease in the peak amplitude with lowering potential could be indicative of a less upright COL configuration while an abrupt change in the FWHM at -1000mV could be adlayer reordering [8]

Next the system with pyridine was studied. CV showed the  $\text{CO}_{\text{ads}}$  was irreversibly adsorbed and a pyridine species reduced at  $-600\text{mV}$ . SFG showed that  $\text{CO}_L$  does not shift, loses intensity, and disappears from  $-700\text{mV}$  onwards (Figure 2, Top). This could be a possible coverage loss, re-orientation, or disordering of adsorbed species. Also noticed was the presence of the C=C aromatic stretch (Figure 2, Bottom), which had potential independent intensity and linewidth shape. No species were noticed for formic acid or the formate anion, which are the thermodynamically favored species. The pyridine is possibly undergoing no molecular re-orientation and could be possible flat on the surface. Measurements in ppp are sensitive to the molecular average tilt [5].

## Conclusions and Future Steps:

The addition of pyridine to the system on Pt electrodes might be in fact blocking  $\text{CO}_2$  adsorption sites leading to higher rates of HER versus organic product formation as reported in literature [3] as the pyridine may be laying flat on the Pt surface. No organic products were seen.  $\text{CO}_{\text{ads}}$  is probably disordered at the surface possibly decreasing the kinetic rate towards organics. In order to further prove that there are no organic species at the interface we would like to probe from  $1200\text{-}1500\text{ cm}^{-1}$  to see if any acetate species form.

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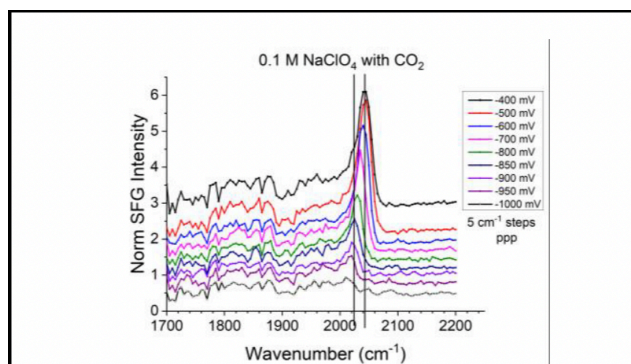


Figure 1: The potential dependent SFG spectra of 0.1 M  $\text{NaClO}_4$  with  $\text{CO}_2$ .

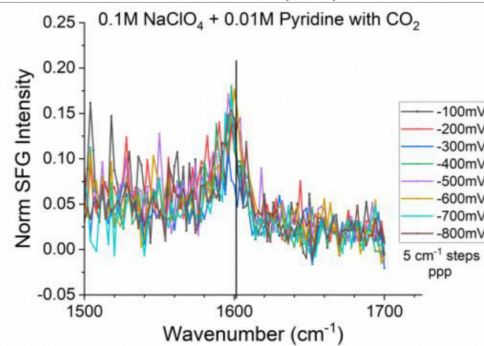
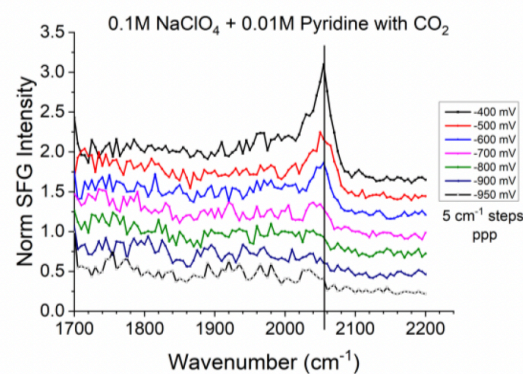


Figure 2: The potential dependent SFG spectra of 0.1 M  $\text{NaClO}_4$  and 0.01M pyridine with  $\text{CO}_2$ .

