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Probing Ethanol Oxidation Mechanism with In-Situ FTIR Spectroscopy via Photodeposited Pt Nanoparticles onto Titania

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Abstract

Hybrid Pt/TiO_2-C catalysts were synthesized via photodeposition in this study in order to increase the kinetics and the carbonate yield of the Ethanol Oxidation Reaction. Photodeposition was chosen because it was believed that the Pt nanoparticles would deposit predominately on top of the oxide sites, which would change the reactivity of the Pt nanoparticles. First, TiO_2-C composites with varying TiO_2 mass percentages were synthesized by sol gel using Vulcan Carbon XC-72R and Titanium Isopropoxide as precursors. The composites were dispersed in isopropanol and mixed with Chloroplatinic Acid such that the final Pt concentration was 20% by weight. This mixture was illuminated with UV light for 3 hours and the Pt/TiO_2-C catalysts were recovered. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis showed that the Pt photodeposition was almost quantitative and XRD patterns showed that the average particle size ranged from 4 to 5 nm. XPS Spectra showed that the Pt nanoparticles shifted to lower binding energies as TiO_2 concentration increased, whereas Ti binding energies shifted to higher values with higher TiO_2 concentrations. The synthesized catalysts showed increased current density in Linear Sweep Voltammetry when compared to a commercial Pt/C catalyst experiments which was attributed to increased nucleophilicity on the Pt which allowed for kinetically easier nucleophilic attacks. In-situ FTIR studies showed that the bands attributed to carbonate vibrations were more intense on the synthesized catalysts. All of these experiments allowed us to conclude that the increased electron density facilitates nucleophilic attacks and C-C bond breaking.

Keywords: EOR, Electrocatalysis, Direct Ethanol Alkaline Fuel Cell, In-situ FTIR