

Electrochemical Methane Activation and Conversion to Oxygenates at Room Temperature

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Methane (CH_4), a plentiful, high energy natural resource and the primary component of natural gas, is inherently difficult to activate due to its lack of polarity and chemical inertness. As a result, high temperatures are typically employed ($\sim 650^\circ\text{C}$ or higher) in fuel cells or reformers to convert CH_4 to syngas and/or other hydrocarbon products [1-3]. However, the drawbacks with such high temperature systems include the cost of high quality heat, stability concerns, and catalyst poisoning and deactivation. As a result, lower temperature alternatives have started to receive increased attention in recent years.

In separate studies, transition metal oxide complexes and Fe-zeolite catalysts were reported to exhibit catalytic activity for CH_4 activation at temperatures at or below 180°C [4,5]. While these heterogeneous chemical systems represent a significant advance, there remains an absence of reports concerning CH_4 activation electrochemically at low temperature. Electrochemical reactors offer distinct advantages over purely chemical ones: i) they are not limited by thermochemical cycles and therefore have a higher theoretical achievable efficiency; ii) the surface free energy can be directly controlled through the electrode potential; and iii) separate, tailorable electrodes allow for non-direct reaction and optimization [6].

Using a bifunctional nickel oxide-zirconia electrocatalyst, CH_4 was activated and oxidized with carbonate anions (CO_3^{2-}) as a source for oxygen donation and charge transfer [7]. Product characterization using Mass Spectrometry (MS), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), and Proton Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$) revealed a myriad of products. Figure 1 shows the products formed in a batch cell collected at 1.8V electrode potential using $^1\text{H-NMR}$. In addition to those shown in Fig. 1, formaldehyde and carbon monoxide were also detected in separate electrochemical cells.

Figure 2 shows the proposed reaction mechanisms for the formation of methanol (CH_3OH) from CH_4 and CO_3^{2-} , and the formation of C-C bonds through C=O bond resonance. This abstraction and donation of oxygen using CO_3^{2-} for electrochemical oxidation is a unique approach and could open up new avenues of low temperature electrochemical CH_4 activation reactors. The effects of different in cell constructions and applied potentials on the

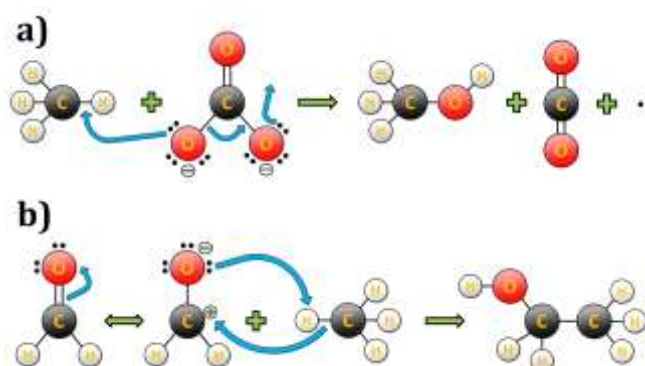


Figure 2 – Proposed reaction mechanisms for a) CH_3OH formation from CH_4 and CO_3^{2-} ; and b) C-C bond synthesis through C=O bond resonance.

product profile observed through MS, ATR-FTIR, and $^1\text{H-NMR}$ will also be investigated and discussed.

$^1\text{H-NMR}$ data shown in this work was collected by Dr. John Flake at Louisiana State University, and we would like to thank him for his collaboration.

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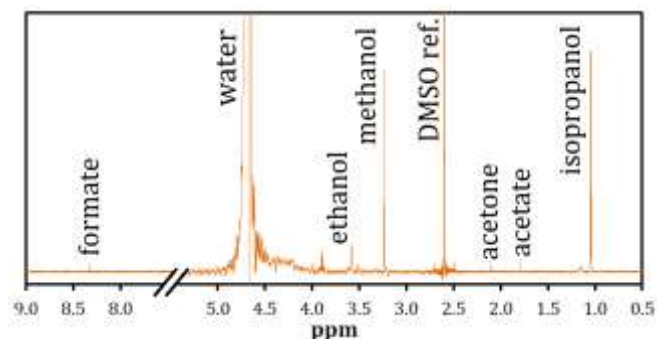


Figure 1 – $^1\text{H-NMR}$ spectrum for aqueous batch cell collected at 1.8V electrode potential.