From Inert Carbon Dioxide to Fuel Methanol by Activation in Plasma Atmosphere

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Abstract. The electron-molecules collisions in plasmas are fructiferous field of study, particularly in activation of inert species into extremely active chemical reactants. Several gases such as carbon dioxide, methane, nitrogen, argon, water among others are ionized or simply activated under collisions with electrons creating the complex atmosphere plasmas. Based upon the energy distribution of electrons and the cross section of molecules it is possible to stimulate molecules becoming highly active species. This research explores the assembly of methanol over a surface of Cu-O-Zr catalyst when carbon dioxide reacts with water under the plasma developed into the Electron Cyclotron Resonance device (ECR). The process was continuously monitored by a mass spectrometer and the correspondent results show the formation of methanol. The ECR operated at 10^{-6} torr assisted with a microwave source of 250 Watts of power; the magnetic field was developed with 300 Amp on Helmholtz coils. The mode of operation of plasma was in cusp, and the electron temperature was 6-eV reported by a single Langmuir probe. The mass spectrometry reported the presence of methanol. The catalysts characterization is reported in form of Scanning Electron Microscopy image, a Raman spectroscopy analysis, and the Electron Dispersive Spectroscopy (EDS).

1. Introduction

The incorporation of physical methods to processes is becoming of great importance and creates positive impact in materials and processing technology. Plasma is incorporated easily in chemistry producing sophisticated molecules. The advantage of the plasma processes is to tune finely the budget of energy to activate chemical reactions and produce valuable materials. In this job research the cross sections of carbon dioxide and water molecules with the distribution of energy of the electrons in the plasma become the reference data to stimulate both molecules; several produced radicals adsorbed over proper catalyst produce methanol. This study is of extremely importance since hydrogen atoms coming from water are being incorporated into carbon structure to produce a chemical stable material. It shows that the hydrogen radicals and hydroxyl radicals react in plasma with carbon dioxide consuming completely the water. Studies of mechanisms of reactions producing methanol reveals in a first step the formation of intermediates formate in which two oxygen atoms from carbon are attached to the zirconium metal atoms [1], [2]. The other steps of assembling are not known since it occurs extremely fast. The studying of methanation of carbon dioxide shows to be feasible since its energy of activation is around 1.0 eV, when hydrogen and carbon dioxide react over the surface of Ni (100) [3]. Similar works using ruthenium catalyst found equivalent activation energy [4]. This energy of activation is relatively low if it is compared with the 6 eV transported by electrons in typical ECR machines. The production of methanol is feasible at relatively low energy of activation since methanol has similar structure as methane. The methanol production results more attractive than methane, because methanol at room conditions is liquid and large amount of hydrogen incorporated in carbon

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can be transported in a safe manner. This present paper demonstrated the feasibility of methanol production starting with carbon dioxide, water and a proper catalyst when the whole system is confined into a carbon dioxide-plasma. Improved plasma reactor could be operated at pilot level, creating high density plasma for large production of methanol.

2. Energy Distribution and mechanisms of the Chemical reaction

Carbon dioxide and water as polyatomic molecules are active in plasmas depending on their electron-collision excitation cross section, their electrons in these molecules are promoted to high energy electronic states, and even electrons could leave the structures forming ions. The Maxwellian energy of distribution of the electrons in the plasma are good reference to predict the probability of interaction between these electrons and polyatomic molecules. The cross section of both molecules has to overlap finding the threshold energy of activation, as shown below [5], [6].

$$\mathbf{e + CO_2 \longrightarrow CO + O\,(^1s)} \qquad \varepsilon_{threshold} = 3.3eV \quad (1)$$

$$\mathbf{e + H_2O \longrightarrow OH + H} \qquad \varepsilon_{threshold} = 5.1eV \quad (2)$$

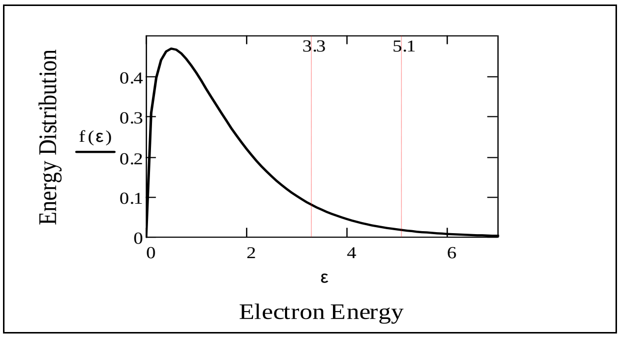


Figure 1. The minimum threshold energy for carbon dioxide and water is 3.3eV and 5.1 eV to interact with electrons in plasma where the typical temperature is about few eV.

The cross sections, of elastic and inelastic collisions are continuously reviewed and updated [1], [2]; for this process the minimum threshold energy related to their cross sections are 3.3 and 5.3 eV. The possible mechanisms of the reaction could be explained as shown below; however the net reaction produces methanol.

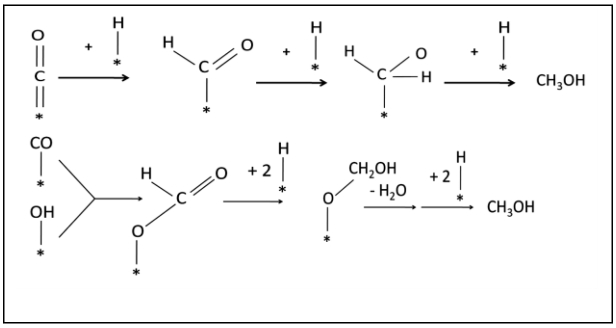


Figure 2. Possible mechanisms of the chemical reaction, the symbol (*) is a possible interaction of species with the solid surface Cu-O-Zr.

3. Methodology

The ECR equipment was used to perform the production of methanol, the equipment reaches a pressure vacuum of 10^{-6} torr. The PUPR Plasma-Cusp Machine required a minimum magnetic field of 0.0875 Tesla for the cyclotron resonance of 2.4 GHz Microwave frequency. Plasma is generated using Electron Cyclotron Resonance Heating (ECRH). This machine could be tuning to generate plasma densities between 10^4 to 10^{12} electrons/cm^3 and electron Temperatures from 0.2eV to 150 eV. For this experiment a microwave power of 250 Watts and 300 Amp of current in the Helmholtz coils that generated the magnetic confinement were used. An electron temperature of 6 eV was measured using a single Langmuir probe. A DME100MS-Dycor Mass Spectrometer is installed in line to monitor the plasma composition. A feedthrough was used to feed water in form of pulses. For each pulse of water a mass spectrum was recorded.

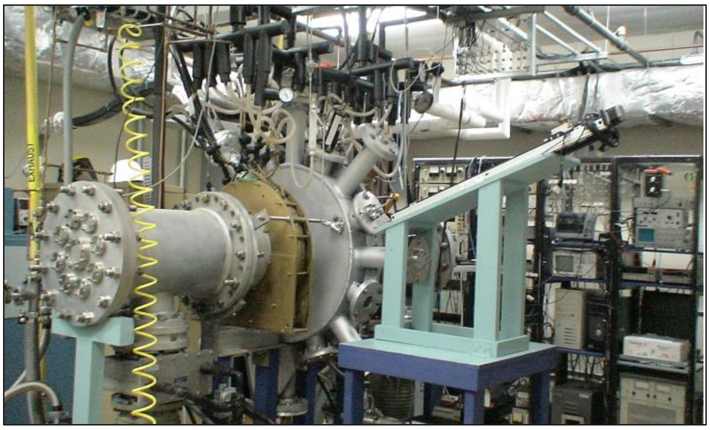
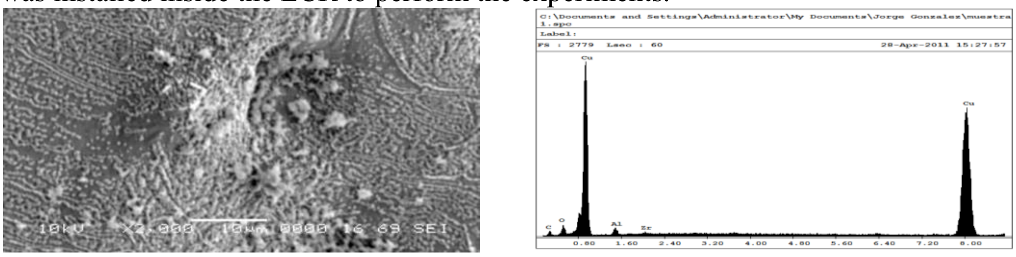


Figure 3. Electron Cyclotron Resonance Plasma Machine at PUPR Polytechnic University of Puerto Rico Plasma Laboratory.[7]

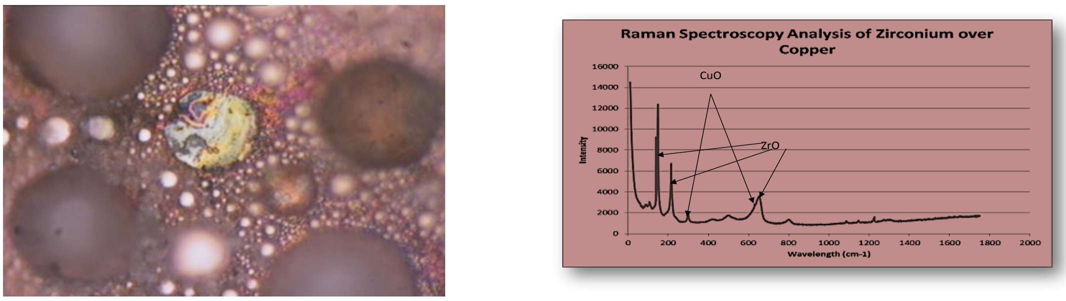
3.1. *Synthesis of the catalyst*

Copper was forced to melt immersed into zirconia, the species were loaded into an alumina tube and the crucible installed into a vacuum chamber was processed at 10^{-3} torr with a stream of hydrogen flowing inside the camber. After melting the material was cleaned with isopropyl alcohol and characterized using Scanning Electron Microscopy (SEM). Figure 4(a) shows the image of Cu-O-Zr by SEM and is clear the uniformly distribution of zirconia spheres over the surface of copper. The testing of EDS shows the presence of Zr and Cu elements shown in Figure 4(b). The Raman spectroscopy indicates the copper oxide formation. Since the atmosphere of the vacuum was hydrogen gas only, then zirconia provided the oxygen to form copper oxide as shown in Figure 5(a) and (b). The catalyst was installed inside the ECR to perform the experiments.



(a) (b)

Figure 4. (a) Uniformly distribution of zirconia over the copper surface and (b) the EDS analysis, showing the presence of Cu and Zr



(a) (b)

Figure 5. (a) Optical Microscopy showing the image of the Cu-O-Zr catalyst × 100 and (b) The Raman spectrum shows the presence of copper oxide

4. Experimental Results

The ECR equipment under controlled parameter provided the carbon dioxide plasma in cusp mode for each experiment. The mass spectrums of the plasma composition were reported after each pulse of water and are reported in Figure 6; methanol is formed only under the presence of water. After consuming the water, carbon monoxide is produced into the ECR device. No presence of hydrocarbons was reported in pure carbon dioxide plasma as shown the spectra in Figure 7.

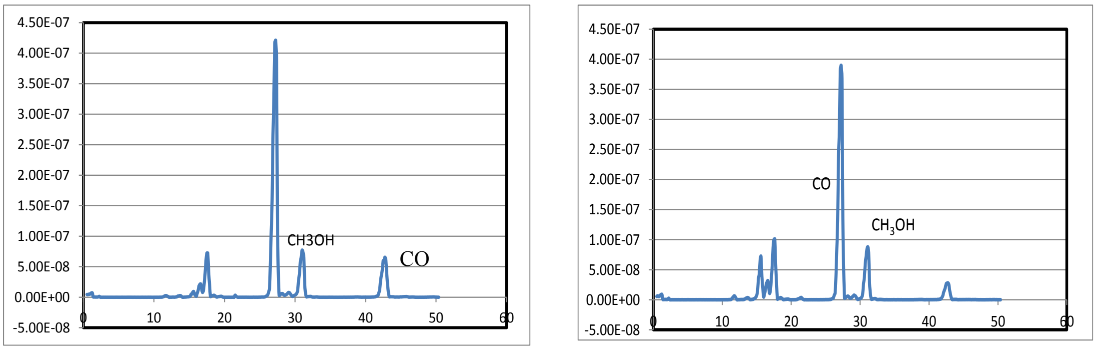


Figure 6. Mass Spectrum of CO_2 plasma after two consecutive pulse of water discharged

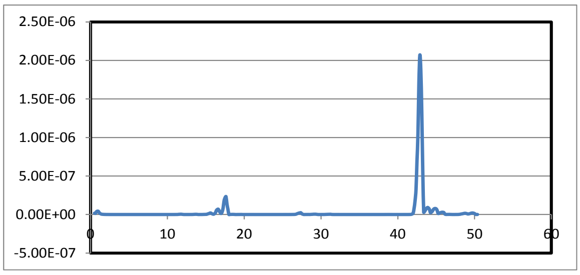


Figure 7. Mass Spectrum of CO_2 Plasma with no pulse of water inside the chamber showing la presence of CO_2.

5. Discussion of Results

Plasma CO_2 is an excellent tool to produce methanol under the presence of Cu-O-Zr catalyst consuming the water. The presence of radicals H and OH produced during the collisions of electron with water molecules produce fast reactions with carbon dioxide. No elemental hydrogen gas is required to be incorporated into carbon structure. Carbon dioxide in excess makes the full consumption of water and carbon monoxide forms as by product due to the limited amount of water during the chemical reaction.

6. Acknowledge

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