Enhancement of Methane Conversion Using Electric Fields

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PROJECT ABSTRACT

The goal of this project is the development of novel, economical, processes for the conversion of natural gas to more valuable products such as methanol, ethylene and other organic oxygenates or higher hydrocarbons. The methodologies of the project are to investigate and develop low temperature electric discharges and electric field-enhanced catalysis for carrying out these conversions. In the case of low temperature discharges, the conversion is carried out at ambient temperature which in effect trades high temperature thermal energy for electric energy as the driving force for conversion. The low operating temperatures relax the thermodynamic constraints on the product distribution found at high temperature and also removes the requirements of large thermal masses required for current technologies. With the electric field-enhanced conversion, the operating temperatures are expected to be below those currently required for such processes as oxidative coupling, thereby allowing for a higher degree of catalytic selectivity while maintaining high activity.

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QUARTERLY OVERVIEW

Experiments continue. In the non-dielectric tubular system, we are still working on some kinetics experiments and also are again doing some catalyst screening, particularly looking for correlations with surface OH and oxygen groups to help determine the manner in which these surfaces alter the selectivities. On the dielectric systems we are looking at power versus frequency and conversions relationships, still working on oxygen utilization (see attached discussion in the appendix) and are building a short residence time reactor (smaller volume) for studying intermediate formation and destruction.

APPENDIX

EXPERIMENTAL SUMMARY OF OXYGEN UTILIZATION PATHWAY STUDIES

SUMMARY OF OXYGEN UTILIZATION PATHWAY EXPERIMENTS

The objective of this research is to determine the oxidative pathways which are produced when methane and oxygen react due to an AC electric discharge. An ozone generator is used to create the AC electric discharge and, thus, allow the reaction to occur. In order to begin the analysis, four types of experiments have been conducted. The first two types of experiments involved varying the flowrate of CO or CO₂ in a methane and oxygen stream whose ratio was three to one. The third type of experiments involved adding both CO and CO₂ to the methane oxygen stream. The last experiments dealt with binary feed mixtures of methane and ethane, helium, carbon monoxide, or carbon dioxide. These experiments proved to be very helpful in the initial mapping of the pathways as well as determine the types of experiments that will have to be conducted in the future. The following discussion will first deal with the conclusions that can be drawn from these studies and then end with the direction in which this research will be going.

The first set of experiments, as already stated, dealt with varying the flowrate of CO in a methane and oxygen stream whose ratio was three to one. In these experiments the methane to oxygen ratio, voltage, frequency, and total feed flowrate were kept constant. The latter three were as follows:

Voltage = 8500 V
Frequency = 100 Hz
Feed Flowrate = 200 cc/min

As the CO flowrate increased, the selectivity of CO decreased while the selectivity of CO₂ increased. With a flowrate of 20 cc/min or greater of CO, the rate of its destruction was greater than the rate of its creation and, thus, produced a selectivity of 0 %. When comparing these CO experimental selectivity results with the results of the experiment which had no CO in the feed, it became quite apparent that the liquid product selectivities remained virtually unaltered. The only exception to this was when the CO feed flowrate was increased to 60 cc/min, then some of the liquid selectivities started to drop off. This happened because, as the CO flowrate increased, the oxygen feed flowrate decreased and, thus, cut down on the production of the oxygenated liquid products. Experiments that will be discussed later on in this paper will show that the oxygen contribution from CO to the liquid products is negligible and, therefore, the presence of oxygen was necessary in order to form these products. Another result of the increase in CO was the increase in selectivity of ethane. At the base case ethane's selectivity was around 4 % while at a 60 cc/min CO flowrate its selectivity jumped to 8 %. Thus, the effect on the activation of methane was not affected as much as the oxidation production. Therefore, the increase in ethane selectivity occurred because the probability of methane coupling goes up when the CO flowrate was increased. Finally, the methane conversion decreased from 20.2%, the base case value, to values which ranged from 17 to 19 percent when CO was inputted into the feed stream. This was because there was less oxygen in the stream which was the major oxygen source for the oxygenated products. This indicated that the oxygenated products are formed by activating oxygen which then in turn activates the methane and, therefore, allows the reaction to take place.

The same set of experiments were run for CO₂, the only difference being that CO₂ took the place of CO in the feed gas. In these experiments, as the CO₂ feed flowrates increased, the CO₂ selectivities decreased while the CO selectivities increased. The liquid selectivities, as was the case in the CO experiments, were unaffected when CO₂ was inputted into the feed stream. The only exception, again, was when the CO₂ flowrate was raised to 60 cc/min. At this flowrate some of the liquid selectivities started to decrease because of the reduced feed oxygen concentration. The CO₂ selectivity became 0 % when the CO₂ feed flowrate was 40 cc/min. This, again, was because the rate of destruction of CO₂ was greater than the rate of creation. The CO₂ experiments showed the same sorts of trends found in the CO runs when talking about ethane selectivity and methane conversion. Here again, limiting the O₂ increased the probability of methane coupling and also demonstrated, through the decrease in methane conversion, that O₂ was the species that had to be activated in order to successfully attack the methane

The third set of experiments dealt with adding both CO and CO₂ to the 3 to 1 methane oxygen stream. The total flowrate, frequency, and voltage were the same as all of the previous ones. When both CO and CO₂ flowrates were set at 17 cc/min, CO₂ selectivity was 15 % while CO's selectivity was 7 %. This suggested the rate going from CO to CO₂ was greater than the rate going from CO₂ to CO at an approximate one minute residence time. The second experiment reduced the CO flowrate to 10 cc/min while keeping the CO₂ flowrate at 17 cc/min. This caused both selectivities to be around 15 %. This was due to the fact that with more CO₂ in the feed stream it caused more CO to be produced as was shown in the CO₂ experiments.

The last set of experiments dealt with binary mixtures of 150 cc/min of methane and 50 cc/min of CO, CO₂, ethane, or helium. The last three of these gases when combined with methane gave ethane selectivities which ranged from 37 % to 57 %. The rest of the products were assumed to be made of C₃+ compounds but at the time the analysis was not available. When methane was the only feed gas, the ethane selectivity was 49 %. It was very interesting to note that the binary mixture of CH₄ and CO₂ produced a total selectivity for liquid products of less than 5 %. This indicated that the contribution of oxygen from the CO₂ to form liquid products was negligible. When methane was flowed with CO, less than two percent of the total selectivity was for liquids. Thus, the same could be said for CO as was said for CO₂. The selectivity for ethane was 82 % when methane and CO were in the feed. This suggests, as was shown in the CO experiments, that CO in the feed stream promotes methane coupling. It seemed to be a better promoter than CO₂ since CO₂ only produced an ethane selectivity of 37 %.

These experiments have shown quite a bit of insight on how the reaction proceeds. However, they do not indicate the order these reactions were occurring. For example, the question of whether methanol and formic acid go on to form methyl formate should be answered. There was some evidence already that CO was formed before CO₂. All the base case methane oxygen experiments showed that CO selectivities were greater than CO₂ selectivities. In order to get a clear idea on what was occurring, however, additional experiments will have to be done. These experiments will deal with varying the residence times of several feed mixtures and determine how the selectivities are altered. To do this a 20 cc reactor will be built in order to allow the mass flow controllers to deliver residence times of less than a second to 30 seconds. Some analysis may be done with a

mass spec., in which case, the carbon or oxygen molecules will have to be labeled. It might be possible to convert the Varian GC to an on line GC. All of the previous experiments that were done had the liquid analysis performed by injecting the condensed product into the Varian GC for analysis. This, however, would be very impractical with the new proposed experiments, because with the decreased residence times it could take days before enough liquid product could be collected. Thus, having the product stream directly go to a GC would be desirable. In this case all of the liquid products would be maintained in the vapor phase when they entered the GC. This would mean a column, such as a CTR column, would have to be used in order to successfully analyze all the products. The liquid products could be calibrated by injecting known amounts of each liquid compound into the GC. Thus, an online GC would analyze the composition of the entire product stream in a relatively short amount of time. Regardless of which method will be implemented, the overall concept will be as the residence time decreases the primary product formed should increase. That is to say, that if the reaction will be an A goes to B goes to C, a decrease in residence time should cause the concentration of B to increase while the concentration of C should decrease.

Another important avenue that needs to be studied is if these C2+ pathways are in parallel or series. If the reactions are in series, then the reaction rates in forming the higher hydrocarbons will not be able to increase as rapidly as the earlier ones. Secondly, the higher hydrocarbons will only start to form when the concentration of the lower hydrocarbons start to build up. If some of the reactions, on the other hand, are in parallel, then rates of increase of two different reaction pathways could be the same. The findings of these new sets of experiments will then determine the direction the project needs to go.