

Kinetic Analysis of Liquid Phase Methane Oxidation

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Introduction

Direct oxidation of methane to methanol has been studied for decades, and has yet to be commercialized. If successful, the process could lead to a decrease of methanol prices in the current methanol market, as well as the opening of new methanol markets in methanol-to-chemical and methanol-to-fuel areas. Two years ago, UOP started a government co-sponsored project (NIST/ATP Award 70NANB4H3041) for selective liquid phase oxidation of methane to methanol. Occasionally the progress of the project was communicated to the scientific community [1,2]. Previously we concentrated on using peroxide as the oxidant for methane oxidation. Recently we have discovered an efficient methane oxidation by air. This presentation covers kinetic analysis of liquid phase oxidation of methane to methanol by air with one of our catalytic systems.

Materials and Methods

Direct methane-to-methanol oxidation was carried out in Parr autoclaves equipped with gas-entrainment impeller. An online GC and UV-vis analysis system was set up to allow for in situ monitoring of reaction kinetics. Typically, pre-catalyst (and promoters sometimes) and solvents were added into a reactor and the reactor then sealed. Methane and air were then added into the sealed reactor. The reactor was then ramped to the desired reaction temperature and then kept at that temperature for a set period of time. The reaction was analyzed by online GC and UV-vis system.

Results and Discussion

It was claimed in the literature that air can be used as the oxidant for direct methane oxidation in trifluoroacetic acid with high efficiency [3]. Through our investigation, we were able to confirm the literature work with one of the transition metal catalysts we screened. In order to understand this system, we have designed an in situ GC and UV-vis analysis system to study the reaction kinetics for one of our catalysts. It was observed that under the reaction conditions the pre-catalyst was transformed into an active catalyst which catalyzed homogeneous methane oxidation to methanol. The reduced catalyst was then re-oxidized by air to complete the catalytic cycle. After a certain period of time, the reaction stopped even though a significant amount of methane and oxygen was still left in the reactor. Online GC analysis showed that the reaction took place in two distinctive stages: active and inactive. In the active stage, the same constant reaction rate was observed for all runs at the same reaction temperature, regardless of whether a promoter was used or not. Analysis of the reaction rate equation showed that the reaction was run under low steady-state catalyst concentration conditions. Online UV-vis analysis was able to observe the active catalyst and confirmed its steady state concentration during the reaction. Even though the catalyst was de-activated

continuously, the low steady state active catalyst concentration, complex reactions among pre-catalyst, catalyst, reduced catalyst, and de-activated catalyst led to a discontinuous change in reactivity. Occasionally, staged reactivity was observed in the literature [4]. This was the first time for us to observe this phenomenon in a liquid phase methane oxidation.

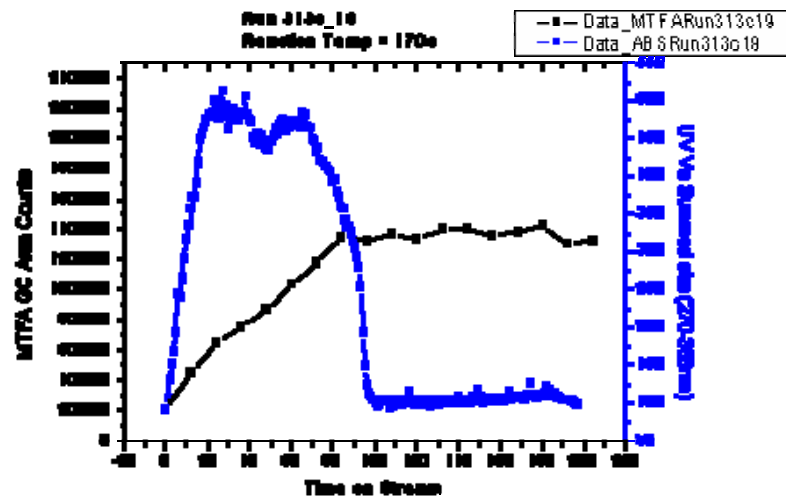


Figure 1. In Situ GC and UV-vis analysis of liquid phase methane-to-methanol oxidation.

In addition, activation energy we obtained (48 kcal/mol) from our kinetic study correlates with a free radical methane activation mechanism.

Significance

Liquid phase oxidation of methane to methanol was found to consist of two sharply defined stages, as analyzed by in-situ GC and UV-vis analysis.

References

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