

## Characterization of catalyst intermediates in Methane Oxidation

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### Introduction

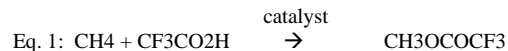
Direct oxidation of methane to methanol has been studied for decades, and has yet to be commercialized. A successful process could lead to a decrease of methanol price in current methanol market, and open new methanol markets in methanol-to-chemical and methanol-to-fuel areas. Two years ago UOP started a government co-sponsored project (NIST/ATP Award 70NANB4H3041) for selective liquid phase oxidation of methane to methanol. The progress of the project has been communicated to the scientific community [1,2]. Recently we have discovered an efficient catalyst for methane oxidation by air. This presentation covers the analysis of the catalyst intermediates that are formed.

### Materials and Methods

Direct methane-to-methanol oxidation was carried out in high pressure Parr autoclaves equipped with stirring. Typically, the catalyst and solvent were added into a reactor and the reactor then sealed. Methane (and sometimes air) was then added into the sealed reactor. The temperature and time of the reaction were then set for the experiment. The liquid and gas products from the reaction were analyzed by GC. Liquid and solid samples from the reaction were also analyzed for metals, phases by XRD, UV-VIS, and Mn K-edge XAFS). A single crystal recovered from the spent reaction solution was used for structure solution by direct methods (Shelxtl Plus) in collaboration with Charlotte Stern at Northwestern University on a Bruker SMART1000 single crystal X-ray diffractometer.

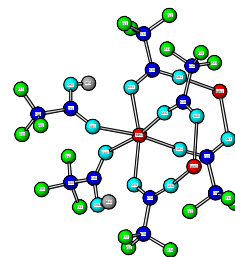
### Results and Discussion

The main reaction being developed is highlighted in equation 1. Methane was reacted with a metal oxide in the presence of a homogeneous transition metal catalyst in trifluoroacetic acid (TFA) to give methyltrifluoroacetate (MTFA) in high selectivity. The reaction was liquid phase, with reaction temperature typically below 200°C.



Fujiwara<sup>3</sup>, Misono<sup>4</sup>, Sen<sup>5</sup>, and others<sup>6</sup> have reported similar reactions utilizing a variety of catalysts and oxidants. We were particularly interested in getting a better understanding of the key catalyst intermediates when metal oxides were used in the presence of TFA solvent with and without oxygen co-feed. Our goal was to develop the understanding of the oxidation state changes of the metal to develop a reversible reaction process. Many catalysts have been investigated and we will report on the findings with Mn<sub>2</sub>O<sub>3</sub>. We investigated the solubility of Mn<sub>2</sub>O<sub>3</sub> in TFA under a variety of temperatures that were studied for reactivity. Under reaction conditions we recovered the Mn complex of the solvent TFA. We will report all of the

findings on our characterization of the Mn and report performance for methane oxidation. The goal of this work was to determine if the system could be regenerated and improved with a small co-feed of air. We have determined the Mn<sup>+2/+3</sup> oxidation states, by a variety of analytical methods, under different reaction conditions. During the course of these experiments we recovered crystals from cooled spent reactions that contained Mn. We will report the crystal structure and discuss this new Mn-species as an intermediate in the solution. We will relate our findings in terms of the reactivity of methane for the formation of MTFA product.



**Figure 1.** Molecular structure of the metal complex recovered from reaction of Mn<sub>2</sub>O<sub>3</sub> in TFA during reaction with methane.

### Significance

Liquid phase oxidation of methane to methanol with Mn<sub>2</sub>O<sub>3</sub> was found to react with the solvent and form a new Mn(TFA) complex. The advancement of the intermediates formed during reaction is an advancement of understanding of the Metal chemistry involved.

### References

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