Semester Project

Synthesis of active solid catalysts for the direct partial oxidation of methane to a methyl derivative

Supervised by Andrea Blankenship (andrea.blankenship@chem.ethz.ch)

The direct selective partial oxidation of methane to products such as methanol is commonly referred to as a "Holy Grail" of catalysis due to the challenges associated with preventing the over-oxidation of the oxygenate products, which greatly diminishes achievable yields[1]. A solution to overcoming this challenge is the protection of methanol within an oxidation-resistant methyl ester[2-4]. Despite the success of such approaches, the translation of this chemistry from a homogeneous catalytic mode to a heterogeneous catalytic mode has been limited[5]. Our group has recently demonstrated an aerobic direct methane partial oxidation process using a heterogeneous silica-supported cobalt catalyst[6].

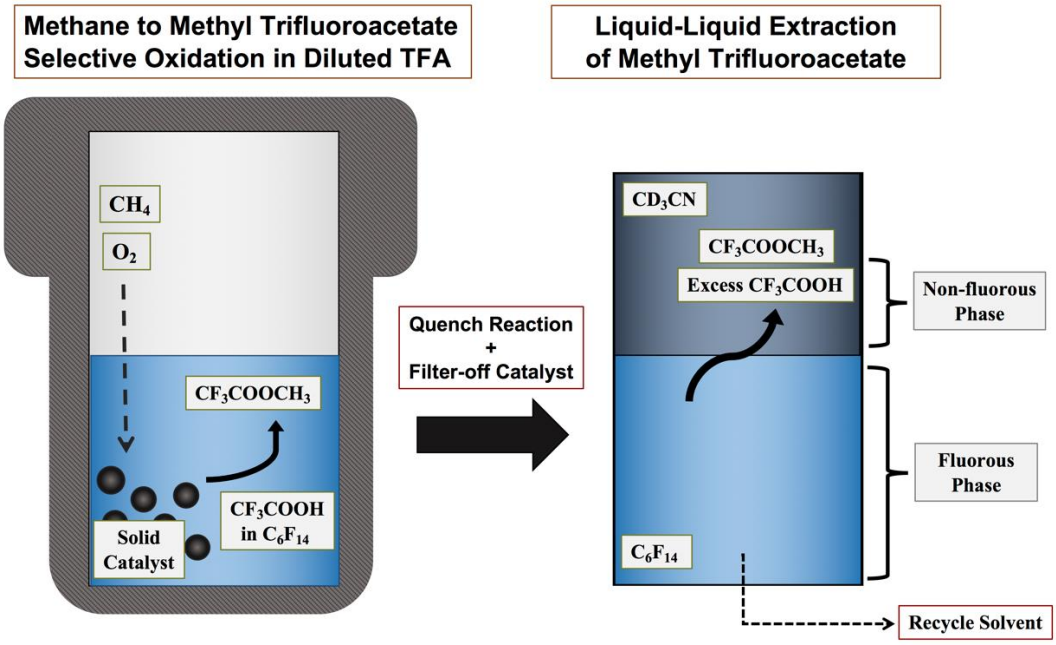

Figure 1: Overview of the designed methane oxidation process and product recovery[6]

The goal of this project is to synthesize, test, and characterize solid catalysts for the direct partial oxidation of methane in the liquid-phase batch system outlined in Figure 1 or a new set-up operating in flow. The student will therefore gain experience in many aspects of catalysis research by performing a variety of tasks related to synthesizing and evaluating catalysts within a relatively short period of time. The student will be responsible for developing their own direction on materials to explore with assistance from the supervisor.

Semester Project

Project Objectives:

1. Perform short literature search on synthesis methods for supported transition metal catalysts
2. Synthesize solid catalysts active
3. Measure catalytic activity of the synthesized catalysts in a batch reactor
4. Characterize synthesized catalysts using relevant methods (XRD, TEM, etc.)
5. Propose structure-activity relationships based on results

Learning Objectives:

1. Develop familiarity with typical synthesis methods for solid supported metal catalysts
2. Strengthen understanding of characterization techniques learned in chemistry curriculum and how they can be applied to heterogeneous catalysis
3. Practice written and oral communication skills

References:

1 Ravi, M., Ranocchiari, M. & van Bokhoven, J. A. The Direct Catalytic Oxidation of Methane to Methanol-A Critical Assessment. *Angew Chem Int Edit* **56**, 16464-16483, doi:10.1002/anie.201702550 (2017).

2 Periana, R. A. *et al.* A Mercury-Catalyzed, High-Yield System for the Oxidation of Methane to Methanol. *Science* **259**, 340-343, doi:10.1126/science.259.5093.340 (1993).

3 Strassner, T., Ahrens, S., Muehlhofer, M., Munz, D. & Zeller, A. Cobalt-Catalyzed Oxidation of Methane to Methyl Trifluoroacetate by Dioxygen. *Eur J Inorg Chem* **2013**, 3659-3663, doi:10.1002/ejic.201300213 (2013).

4 Ravi, M. & van Bokhoven, J. A. Homogeneous Copper-Catalyzed Conversion of Methane to Methyl Trifluoroacetate in High Yield at Low Pressure. *Chemcatchem* **10**, 2383-2386, doi:10.1002/cctc.201800412 (2018).

5 Palkovits, R., Antonietti, M., Kuhn, P., Thomas, A. & Schuth, F. Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol. *Angew Chem Int Edit* **48**, 6909-6912, doi:10.1002/anie.200902009 (2009).

6 Blankenship, A., Ravi, M., Newton, M. A. & van Bokhoven, J. A. Manuscript in progress.