Semester Project

Exploration of methanol recovery from methyl trifluoroacetate from the syngas-free partial oxidation of methane

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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, outlined in Figure 1[6].

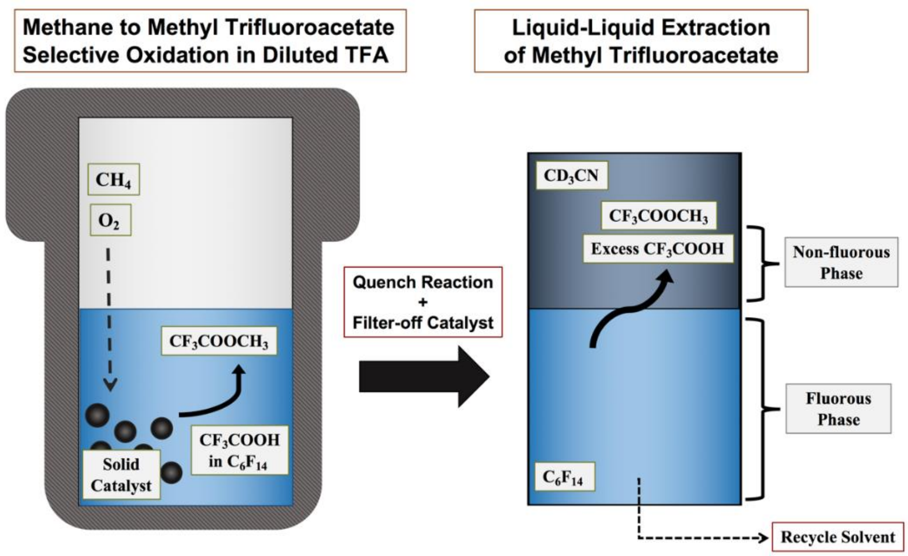

Figure 1: Overview of the designed methane oxidation process and product recovery from the fluorous phase[6].

A crucial aspect affecting the practicality of this methane-to-methyl-ester (MtME) process is the ability to recover methanol from methyl trifluoroacetate via hydrolysis. Thorough consideration of this recovery step has been largely disregarded, despite the fact that the reaction kinetics and required conditions have a significant impact on the overall productivity of these systems. Therefore, the goal of this semester project is to evaluate the relevant reaction timescales pertaining to the recovery of methanol from methyl trifluoroacetate. The student will therefore gain experience in many aspects of catalysis research by experimentally determining apparent reaction kinetics in addition to screening solid catalysts. The student will be responsible for developing their experimental plan with assistance from the supervisor.

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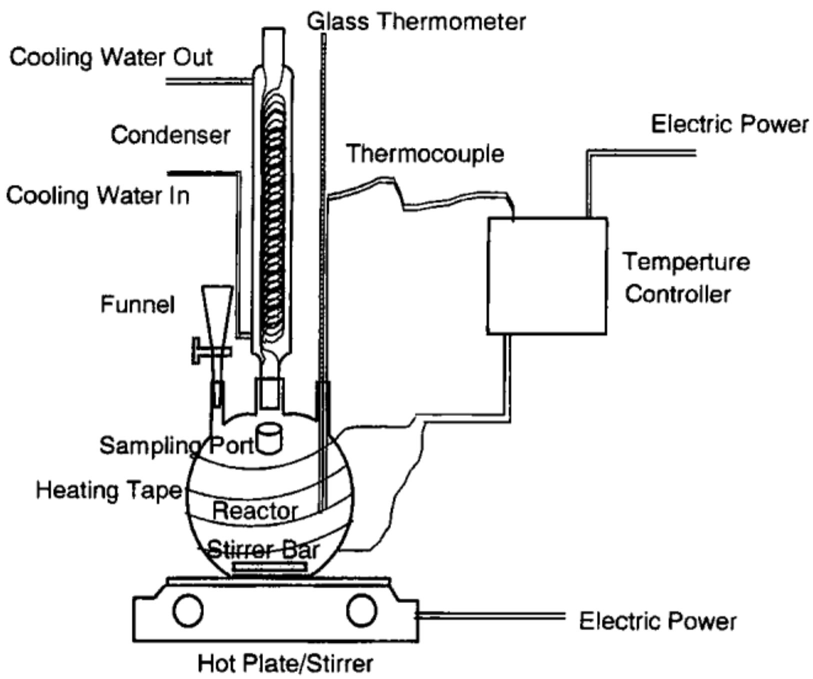

Figure 2: Example of the apparatus required for hydrolysis experiments.[7]

Project Objectives:

1. Perform short literature search on potential catalysts for ester hydrolysis.
2. Assemble apparatus and write relevant safety and operating procedures.
3. Select and characterize catalysts for ester hydrolysis.
4. Measure reaction timescales of ester hydrolysis with and without catalysts.
5. Determine hydrolysis conditions and catalysts required to reach process productivity targets.
6. Provide outlook on the feasibility of methanol recovery from methyl trifluoroacetate relevant for MtME systems.

Learning Objectives:

1. Organization and formulation of tasks and objectives on a weekly basis in a way that makes optimal use of available time and resources.
2. Strengthen understanding of kinetics and catalyst characterization learned in chemistry/chemical engineering curriculum.
3. Interpret experimental results and apply findings to the “big picture”
4. Practice written and oral communication skills.

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References:

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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. N., Ravi, M., Newton, M. A. & van Bokhoven, J. A. Heterogeneously Catalyzed Aerobic Oxidation of Methane to a Methyl Derivative. *Angewandte Chemie International Edition* **60**, 18138-18143, doi:10.1002/anie.202104153 (2021).

7 Xu, Z. P. & Chuang, K. T. Kinetics of acetic acid esterification over ion exchange catalysts. *The Canadian Journal of Chemical Engineering* **74**, 493-500, doi:10.1002/cjce.5450740409 (1996).