Autothermal Oxidative Coupling of Methane

West, David[1*], Liang, Wugeng[1]; Sarsani, Sagar[1]; Balakotaiah, Vemuri[2]

1 SABIC, Sugarland, Texas 77478; 2 Department of Chemical and Biomolecular Engineering

University of Houston, Houston, Texas 77204

**Corresponding author: dwest@sabic.com*

Highlights

- Autothermal operation with room temperature feed is demonstrated experimentally.
- Necessary conditions for autothermal operation are analyzed using bifurcation theory.
- Heat loss and diffusion limitations reduce the feasible region for autothermal operation.

1. Introduction

Since 1982 scientists have searched for better catalysts for oxidative coupling of methane (OCM) with the goal of finding one capable of high (>30%) methane conversion and high selectivity to ethylene. This research appears to be predicated on the notion that, once found, such a catalyst could be scaled up using a cooled multi-tubular reactor. For a commercial reactor the methane conversion is limited by the ability to remove heat on the time scale of the reaction. This problem was identified by Dautzenberg *et al*. [1] in 1992 and later by Hoebink *et al*. [2] in 1994, but has been largely ignored ever since. Here we report the exploitation of thermal effects and bifurcation (ignition and extinction) behavior to enable steady-state operation of an OCM reactor with ambient feed temperature and without any external heating after startup. With this approach, the reactor is operated nearly adiabatically. The low temperature feed provides the cooling necessary to control the catalyst at the optimal temperature, effectively solving the heat removal problem. To do this successfully, the reactor must be operated in the region of steady-state multiplicity, on the ignited branch. Consequently, the maximum per-pass methane conversion that can be obtained using this strategy is determined by the extinction point. In typical laboratory experiments there is a large amount of heat loss from the reactor tube which produces a number of interesting effects, for example, an isolated ignited branch exists over a wide range of space velocities and conversion may increase with increasing space velocity. Using a simplified kinetic and reactor model and results from bifurcation theory, we explain the experimentally observed ignition-extinction behavior for reactor tubes of varying diameter when the furnace temperature or the space time are varied. We apply the theory to analyze the impact of reactor tube diameter and heat loss on the feasible region of autothermal operation and present experimental evidence for the existence of an isolated high conversion branch. The results indicate that when catalyst activity is high enough, it is possible to operate an OCM reactor autothermally using the reactor feed (at ambient temperature or even lower) as coolant, which enables the maximum practical single-pass methane conversion. Previously we showed that autothermal operation is feasible but only obtained low C_2+ selectivity [3]. Here we present the first results for autothermal OCM with good selectivity.

2. Methods

Experiments were carried out in fixed bed reactors made of fused quartz tubing of various inside diameter ranging from 2.3 to 50.8 mm. Very thin packed beds were used in order to simplify the analysis of the results. Reactant gas flows were controlled using Bronkorhst Thermal Mass Flow Controllers. A small quantity of neon or helium gas was mixed with the CH4 and O2 for use as an internal standard (the combined feed typically contained 1–3% of inert gas). No other diluents were used. The reactors were heated using a conventional tube furnace. The reactor effluent was analyzed directly (without water removal) using an Agilent 6890 gas chromatograph equipped with two columns and flame ionization and thermal conductivity detectors. In some cases for faster analysis, the effluent was air cooled and water removed by a small knock-out vessel, then passed through a Genie membrane filter and analyzed using an Agilent micro GC. A simple lumped parameter kinetic model was developed by fitting the kinetic parameters to the ignition and extinction points. A CSTR model was used to describe the reactor; this is valid in the limit of very short catalyst bed depth. La-Ce oxide powder catalyst with 15:1 La/Ce mass ratio was prepared and calcined at 625 ^{o}C for 5 hours prior to use. The final powder consisted of irregular particles with number average diameter of 11 µm (determined by SEM) and BET surface area of 15.7 m^2/g.

3. Results and discussion

Large heat losses are present in laboratory scale reactors due to their high surface to volume ratio. This reduces the size of the feasible region for autothermal operation. Figure 1 shows the feasible region for autothermal operation using ambient feed temperature in the plane of adiabatic temperature rise and contact time for laboratory reactors with 10.5 and 34 mm i.d. The region for an adiabatic reactor is shown for comparison. The two stars indicate points at which our experiments were done. The feasible region of autothermal operation is determined by the extinction point. For a non-adiabatic reactor there are two extinction points (see the red and green curves). The left side of the red and green curves corresponds to the blow-out point where the rate of heat removal by flow exceeds the rate of heat generation by reaction and the rate of heat loss through the reactor wall is small. The right side of the two curves correspond to extinction because of too high rate of heat removal by radiative and convective losses (in the radial direction) through the reactor walls.

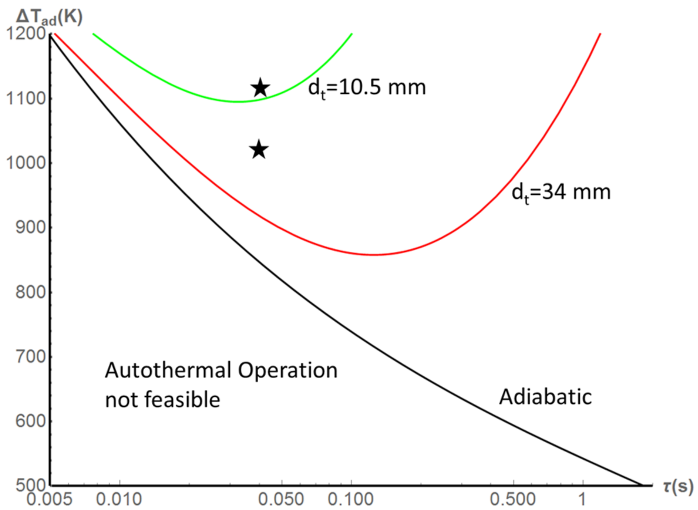

Figure 1. Feasible region for autothermal operation for lab scale and adiabatic reactors.

4. Conclusions

We experimentally demonstrate, for the first time, stable autothermal operation with high ethane/ethylene selectivity in a laboratory scale reactor. We also present experimental evidence of operation on an isolated ignited branch with OCM. We compare our results with those of a simplified model, and use it to illustrate the necessary conditions for autothermal operation with maximum per-pass methane conversion.

References

[1] F. M. Dautzenberg, J. C. Schlatter, J. M. Fox, J. R. Rostrup-Nielsen, L. J. Christiansen, Catal. Today 13 (1992) 503–509.
[2] J.H.B.J. Hoebink, P.M. Couwenberg, G.B. Marin, Chem. Eng. Sci. 49 (1994) 5453–5463.
[3] S. Sarsani, D. West, W. Liang, V. Balakotaiah, Chem. Eng. J. 328 (2017) 484–496.

Keywords
Autothermal, ignition, extinction, bifurcation.