Autothermal oxidative coupling of methane with ambient feed temperature

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HIGHLIGHTS

- Oxidative coupling of methane with ambient feed temperature is demonstrated.
- Ignition and extinction behavior with varying CH_4/O_2 ratio is explained.
- Impact of reactor tube diameter on observed ignition-extinction behavior is analyzed.
- The feasible region of autothermal operation with ambient feed temperature is identified.
- Ignition-extinction behavior of catalysts with different activities are compared.

GRAPHICAL ABSTRACT

Photograph of laboratory scale oxidative coupling of methane reactor operating with ambient feed temperature and without external heating. The catalyst (La-Ce oxide) powder is sandwiched between quartz particles.
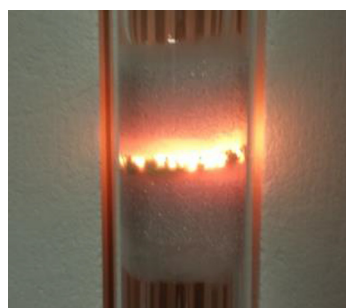
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ABSTRACT

We report the exploitation of thermal effects and bifurcation (ignition and extinction) behavior to enable steady-state operation of an Oxidative Coupling of Methane (OCM) reactor with *ambient* feed and furnace temperature. Using a simplified kinetic and reactor model and results from bifurcation theory, we explain the experimentally observed ignition-extinction behavior for catalysts of different activity and 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 isolated high temperature/conversion branches. 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 lower) as coolant, which enables the maximum practical single-pass methane conversion.

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1. Introduction

The shale gas revolution has made low cost natural gas abundant, encouraging renewed interest in natural gas conversion to useful chemicals. Oxidative Coupling of Methane (OCM) is a poten-tial route for direct conversion of methane to C_2 and higher hydro-carbons (i.e., C_2+ hydrocarbons). It has perhaps the highest carbon atom efficiency of any known route for methane conversion to chemicals. OCM has been extensively studied since first reported by Keller and Bhasin [1] in 1982, with more than 2700 papers and 140 patents published [2]. Many publications have focused on the development of catalysts with high C_2+ yield. The search for high yield catalysts was likely motivated by an early economic

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analysis that suggested a minimum target of 35% per-pass methane conversion and 88% C_2+ selectivity is needed for manufacturing cost competitiveness [3]. However, in addition to good economics a commercial process must first be *feasible*.

Some basic practical engineering problems must be solved before the scale-up and commercialization of OCM is even feasible. The reactions between methane and oxygen leading to C_2+ products are highly exothermic, while the complete oxidation reactions of methane or C_2+ products (to CO_2 and H_2O) are even more exothermic. It is also well known that there is an optimum catalyst temperature range in which C_2+ product selectivity is maximized; this is in the range 1050–1200 K, depending on the catalyst [4,5]. At suboptimal temperatures oxygenated products are formed, while at too high temperature gasification and deep oxidation of the C_2 products take over. Moreover, catalyst deactivation occurs at too high temperature. Maximizing the profit of an industrial OCM process requires operation at the optimal selectivity with as high methane conversion as possible. Consequently, the catalyst temperature must be controlled at some optimal and possibly narrow range. The high heat of reaction of OCM requires limiting the methane conversion to a relatively low value in order to avoid a runaway reaction [6,7]. Hoebink et al. [7] showed that a cooled multi-tubular reactor capable of avoiding runaway is not commercially feasible. Even with a methane to oxygen ratio of 10, it would require about 12 million tubes for a world scale ethylene plant (1000 kTA). Schweer et al. [4] determined the limits of stability and performance of a laboratory scale non-isothermal fixed bed reactor cooled or heated by a fluidized sand bath. They found that a temperature of 853 K was required to initiate the reaction and observed large axial temperature gradients, as high as 250 K. Controlling the maximum hot-spot temperature within their catalyst to less than 1273 K required limiting the inlet oxygen concentration to 20% ($O_2/CH_4 = 0.25$). In order to increase total oxygen concentration (to 30%), C_2+ yield, and methane conversion, they used two reactors in series with interstage cooling and distributed oxygen feed. However, the maximum methane conversion obtained was about 31% for both co-feed and distributed feed operation. Similarly both modes of operation obtained the same maximum C_2+ selectivity, showing no benefit of distributed feed operation. Even if this approach had been successful in increasing methane conversion and selectivity at the laboratory scale, it could not possibly be scaled up to industrial scale given the results of Hoebink et al. [7]. Likewise, an adiabatic reactor with feed temperature of 853 K and 20% O_2 is not feasible either, because the adiabatic temperature rise is about 1000–1100 K for $O_2/CH_4 = 0.25$. Clearly no catalyst could withstand the adiabatic temperature (about 1900 K).

The main focus of this paper is on demonstrating the feasibility of doing OCM in an adiabatic (or near-adiabatic) autothermal reactor and on defining the necessary conditions for this mode of operation. We use the term autothermal to describe intentional operation within the region of steady-state multiplicity in which most or all of the catalyst bed is in an ignited state. Once ignited no further input of heat is used. The maximum benefit of autothermal operation is obtained when reactants are fed at the lowest possible temperature which enables the highest possible methane conversion. This basic concept was demonstrated by Tarasov and Kustov in a 10 mm i.d., vacuum jacketed, laboratory reactor using 15% La_2O_3 on MgO catalyst for short periods of time (about one hour) [8]. However, in their experiment the reaction extinguished within about 20 min after the vacuum insulation was released. We will show that autothermal operation requires understanding of the ignition and extinction behavior and external heat transfer characteristics of the catalyst/reactor system. In the remaining part of the introduction we will review previous work in which ignition and extinction have been observed.

Several groups have measured hot spot temperatures within the catalyst bed in laboratory scale testing that exceed the feed or furnace temperature by 150–300 °C [4,9,10]. Annapragada and Gulari [11] first reported *ignition* and *hysteresis* behavior in OCM. On increasing furnace temperature they observed ignition at 725 °C, with sustained activity on reducing furnace temperature to 575 °C. Using pelletized $Mn-Na_2WO_4/SiO_2$ catalyst and a space time of 0.36 s, Lee et al. [12] observed ignition in a 25.4 mm diameter reactor tube at ~780 °C and hysteresis on cooling, with extinction at a furnace temperature of about 660 °C. However, in order to limit the maximum catalyst temperature the reactants were diluted with N_2 (60%). More recently, Noon et al. [13] reported a significantly lower ignition temperature of 520 °C and sustained activity down to 230 °C with a La-Ce oxide nano-fiber catalyst (with much lower space times, about 0.01 s). Comparing nano-fiber and powder catalysts under the same conditions, the observed ignition temperature was 90 degrees lower for the nano-fiber catalyst. The authors speculated that the lower ignition temperature may be due to differences in the crystal structure and porosity produced during the rapid electrospinning process used to synthesize the nano-fiber catalyst.

The ignition and extinction behavior of highly exothermic catalytic reactions in flow systems has been studied extensively both experimentally and theoretically in the past fifty years. A recent review [14] discussed thermal effects expected in catalytic partial oxidations and gave simple criteria for when they are expected. This article also presented some general results on the impact of adiabatic temperature rise, catalyst activity, feed temperature, space time, characteristic heat removal time, external mass transfer and intra-particle diffusional limitations on the ignition and extinction behavior of reactors in which partial oxidation reactions occur. Some of these results are extended and used in the interpretation of the experimental data presented in this work. While the basic theory is not new, this is the first time it has been presented in dimensional form and applied to oxidative coupling.

In the remaining sections we present examples of experimental bifurcation diagrams using furnace temperature and space time as bifurcation variables. We interpret these behaviors using theory and analyze the effects of tube diameter and importance of catalytic activity on the bifurcation behavior and its impact on the feasible region for autothermal operation. Finally, we show two examples of stable autothermal operation in laboratory reactors without any external heating and with reactants fed at ambient temperature.

2. Material and methods

2.1. La-Ce oxide catalyst

Except where noted, the inorganic materials were obtained from Sigma Aldrich Chemical Company with purity of 99.9%. La-Ce oxide powder catalyst with 15:1 La/Ce mass ratio was prepared by combining aqueous solutions of $La(NO_3)_3$ $6H_2O$ (24.85 g dissolved in 40 ml of deionized water) and $Ce(NO_3)_3$ $6H_2O$ (1.65 g in 10 ml of water) and heating at 85 °C for 2 h with stirring. The obtained mixture was dried overnight at 125 °C to yield a dry powder, which was then calcined at 625 °C for 5 h 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, measured using a Quantachrome Autosorb®-6iSA. The sample was outgassed at 300 °C for 4 h before measurement. The XRD pattern of the catalyst is shown in Fig. 1a. XRD measurements were performed with PANalytical X'Pert (Cu $K_{\alpha 1}$ X-ray source,