

IGNITION AND EXTINCTION ANALYSIS OF METHANE OXIDATIVE COUPLING WITH $\text{La}_2\text{O}_3/\text{CAO}$ CATALYST

Zhe Sun¹, David H. West², and Vemuri Balakotaiah^{1*}

¹University of Houston, Houston, TX 77004, Email: bala@uh.edu

²SABIC Technology Center, Sugarland, TX 77478, Email: dwest@SABIC.com

Abstract

The experimentally observed ignition-extinction behavior of highly exothermic Oxidative Coupling of Methane (OCM) with $\text{La}_2\text{O}_3/\text{CaO}$ catalyst is explained by applying the bifurcation techniques and using a global kinetic model. In laboratory-scale packed bed reactors, the ignition-extinction behavior can occur either at the reactor or particle level. The extinction point (which forms the boundary of the region of autothermal operation) is parametrically sensitive. The location of the extinction point is determined by the integrative impact of inter and intra-particle heat/mass dispersion, operating conditions and kinetics of the oxidation reactions. We present analysis and simulations on the impact of these parameters on catalytic OCM in packed-bed reactors.

Keywords

Ignition, Extinction, Autothermal operation, Oxidative coupling of methane, Intra/Inter-particle diffusion

Introduction

Oxidative coupling of methane (OCM) is an attractive route for the direct conversion of methane into value added products. The highly exothermic feature of OCM system leads to complex ignition-extinction behaviors, different reactant conversion as well as product distribution under the same operating condition. The ignition-extinction behavior of OCM was firstly observed experimentally by Annapragada and Gulari (1990), and then also reported by many other groups. These studies on the hysteresis behaviors motivated the investigation of autothermal operation of OCM system. With autothermal operation, there is no heat addition to the reactor and there is no intentional heat removal by cooling. The existence of multiple steady-state is essential for autothermal operation with low feed (furnace) temperature and space time. Recently, Sarsani et al. (2017) presented experimental data on the autothermal operation of laboratory scale reactors with La-Ce oxide under ambient feed (and furnace) temperature. Our previous works discussed the hysteresis behaviors of gas phase OCM reactions by developing a

nine-step global kinetics (Sun et al., 2018). We also showed the general ignition-extinction features of catalytic OCM in laboratory-scale packed-bed reactors with powdered catalyst for the case of single and multiple oxidation reactions (Sun et al., 2018). Although the simplified kinetic model is sufficient to explain the ignition-extinction behavior, it cannot be used to predict detailed product distribution. Further, the assumption of powdered catalyst and neglect of inter and intra-phase gradients is not always valid in a practical system. The main goal of this work is to present a comprehensive bifurcation study which includes various oxidation, reforming and water gas shift reactions, using an experimentally validated kinetic scheme by Stansch et al. (1997) for $\text{La}_2\text{O}_3/\text{CaO}$ catalyst. The present work emphasizes the impact of following factors on the ignition-extinction behavior and the C_2 product selectivity in catalytic OCM systems: 1) competition of various reactions along the steady-state ignition-extinction curve; 2) heat and mass dispersion in the catalyst bed; 3) inter-phase heat and mass transfer and intra-particle concentration

* To whom all correspondence should be addressed

gradients; 4) experimental conditions (flow rate, feed composition, and feed temperature and so forth). The possibility of autothermal operation by $\text{La}_2\text{O}_3\text{-CaO}$ catalyst will also be discussed.

Results and discussion

Fig. 1 shows the adiabatic steady state exit C_2 product selectivity versus furnace temperature for different catalyst bed depths. For a fixed bed depth, complex bifurcation behaviors are observed even in the adiabatic cases due to different characteristic times of various reactions in the system. On the unignited branch, the selectivity towards C_2 product is low and the primary oxidation reactions forming CO_x are dominating in the system. However, with the same feed temperature, an ignited branch with high C_2 product selectivity exists due to the presence of the region of multiplicity. On the ignited branch, the dimerization reaction forming C_2 products dominates among all oxidation reactions. As the feed temperature and catalyst temperature keep increasing, the deep oxidation and reforming of C_2 products become significant, resulting in a drop in C_2 selectivity. Fig. 1 also shows a non-monotonic change of the extinction point as bed depth decreases. Bed depth of 2 mm gives the largest region of multiplicity due to the unequal heat and mass dispersion inside the catalyst bed. The strong heat dispersion results in relatively flat temperature profile inside the catalyst bed while the large concentration gradient still exists. The strong concentration gradient of limiting reactant (oxygen) also results in a decrease in C_2 selectivity with increasing bed depth.

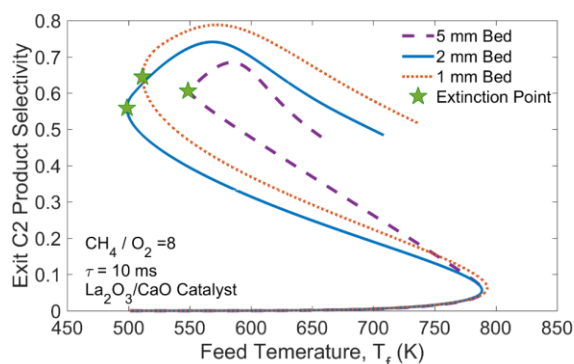


Figure 1. Impact of bed depth on ignition-extinction and C_2 product selectivity.

The multiplicity can also be generated by the ignition of a single catalyst particle when the particle size is large and inter-phase temperature gradient is significant. Fig. 2 shows the ignition of a single particle with and without intra-particle diffusion effect. When the intra-particle diffusion is not present, an ignited branch with locally high selectivity towards C_2 is observed due to the unequal inter-phase mass transfer time of different species (locally high CH_4 to O_2 ratio). However, when intra-particle diffusion is

present in the solid phase, both region of multiplicity and C_2 product selectivity is reduced due to pore diffusional limitations.

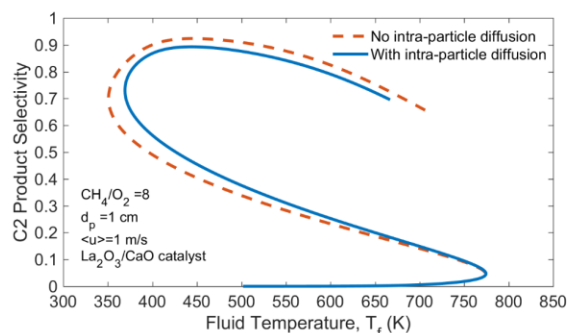


Figure 2. Steady-state ignition-extinction of a single particle.

Conclusions

We present a complete bifurcation analysis of catalytic OCM reaction using a global kinetic model for the $\text{La}_2\text{O}_3\text{-CaO}$ catalyst. The ignition-extinction behavior and detailed product distribution are analyzed for both powdered catalyst beds and packed-bed reactors with large particles. For both cases, the best C_2 selectivity is achieved on the ignited branch close to the extinction points, where the dimerization reaction dominates all other oxidation reactions. The reforming and secondary oxidation reactions kick in as temperature increases further. For the powdered catalyst, the existence of an ignited branch and the product distribution on the ignited branch is strongly influenced by the heat and mass dispersion in the bed. For beds with larger particles, the behavior on the ignited branch is more impacted by the gas to particle heat and mass transfer. It is also shown that the autothermal operation with ambient feed/furnace temperature is feasible for $\text{La}_2\text{O}_3\text{-CaO}$ catalyst under practical operating conditions.

References

- Annappagada, A. V., Gulari, E. (1990). Fe-P-O Catalysts for Methane Utilization-Catalyst Development and Identification. *J. Catal.*, 123, 130.
- Sarsani, S., West, D. H., Liang, W., Balakotaiah, V. (2017). Autothermal Oxidative Coupling of Methane with Ambient Feed Temperature. *Chem. Eng. J.*, 328, 484.
- Stansch, Z., Mleczko, L., Baerns, M. (1997). Comprehensive Kinetics of Oxidative Coupling of Methane over the $\text{La}_2\text{O}_3\text{/CaO}$ Catalyst. *Ind. Eng. Chem. Res.*, 36, 2568.
- Sun, Z., Kota, A., Sarsani, S., West, D. H., Balakotaiah, V. (2018). Bifurcation Analysis of Methane Oxidative Coupling without Catalyst. *Chem. Eng. J.*, 343, 770.
- Sun, Z., West, D. H., Balakotaiah, V. (2018) Bifurcation Analysis of Catalytic Partial Oxidations in Laboratory-Scale Packed-Bed Reactors with Heat Exchange. *Chem. Eng. J.*, doi:10.1016/j.ccej.2018.08.151.