KINETIC STUDY OF OXIDATIVE COUPLING OF METHANE OVER SR-CE-YB-O CATALYST

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Abstract

A comprehensive kinetic study of the oxidative coupling of methane to higher hydrocarbons over a Sr-Ce-Yb-O catalyst was conducted in a differential packed-bed reactor covering a wide range of temperature, concentration and flow conditions (600 < T < 850 °C, 2 < p_{O_2} < 11 kPa, 23 < p_{CH_4} < 93 kPa, 3.33 < m_{cat}/F_v^{STP} < 333 kg.s/m^3). Methods including the usage of a fluidized sand bath, fine catalyst particles and dilution in both feed and catalyst bed are used to ensure the measured reaction rates are not influenced by mass transfer limitation and thermal effects. From the experimental data, we developed a global kinetic model consisting of three primary and four consecutive reactions, which is capable of capturing all qualitative behaviors of the reaction system with good quantitative accuracy.

Keywords

Oxidative coupling of methane, Kinetic modeling, Natural gas

Introduction

Since the initial work of Keller and Bhasin (1982), the oxidative coupling of methane (OCM) to higher hydrocarbons has generated intense interest. The decrease of natural gas prices in the United States during the last decade due to shale gas has increased the economic incentives to develop new outlets for methane and driven further interest in OCM. In order to explore possible OCM reactor designs that are economically viable, it is desirable to understand the intrinsic kinetics of the reaction system. However, given the high temperature, large heat of reaction, and high reaction rate, it is difficult to obtain kinetic data that are not complicated by mass transfer and thermal effects. Our goal is to use a sand bath reactor, similar to the reactor of Stansch et al. (1997), to obtain isothermal kinetic data that are unaffected by these complications. With intrinsic kinetic data, we can develop a global kinetic model that not only describes the kinetic data, but also can be extended through the inclusion of physical effects to predict behavior under conditions where mass transfer and thermal effects are important.

Experimental Design

Catalyst

The composition of the Sr-Ce-Yb-O catalyst tested in this work can be characterized by an overall general formula as $Sr_{1.0}Yb_{0.9}Ce_{0.1}O_y$. Details of the catalyst including its synthesis can be found in Liang et al. (2018). In the kinetic measurements, catalyst particles with diameters 0.25-0.42 mm were applied.

Reactor

A quartz U-tube reactor with an ID of 2.3 mm is used for the kinetic experiments (see Figure 1). To suppress homogeneous gas-phase reactions before and after the

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catalyst bed, quartz rod fillers with an OD of 1.5 mm are used in the straight portions of the tube, while quartz chip fillers are used in the U bend. To minimize temperature gradients, the catalyst particles were diluted with quartz chips. To ensure isothermality of the reactor, the U-tube reactor is immersed in a fluidized sand bath.

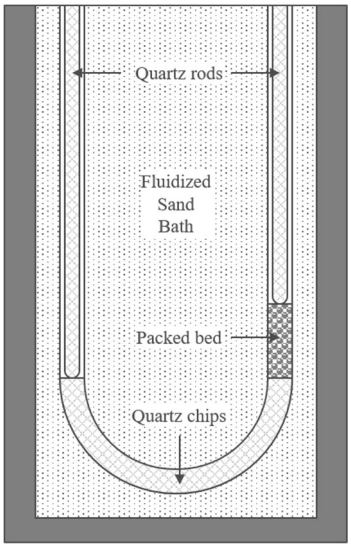

Figure 1. Schematic of the fluidized sand bath reactor (not drawn to scale).

Testing Procedure

We defined a base condition at a temperature of 700°C, total flow rate of 54 sccm with base concentration condition at 44.4% CH_4, 5.6% O_2, 47.2% N_2 and 2.8% He. The usage of diluent in the feed gas helps control the overall reaction and heat generation rate, while it also provides the ability to vary the concentrations of CH_4 and O_2 individually.

At the beginning of each run, the catalyst is tested at the base condition before going to the desired temperature. At each temperature, variations of total flow rate, individual CH_4 and O_2 concentrations and total diluent are tested in blocks of conditions. At the end of each run, the reactor returns to the base condition to check for catalyst aging and other run-to-run variations.

Experimental Results and Model Development

Experiments are conducted over a wide range of operating conditions. As an example, the results at 700°C are summarized in Figure 2, showing how O_2 conversion and 'C' selectivity changes with total flow, CH_4, O_2 and diluent concentration variations. Based on the experimental observations, a global kinetic model consisting of three primary and four consecutive reactions is proposed to describe the reaction system (see Table 1). As shown in Figure 2, the model has very good agreement with the data.

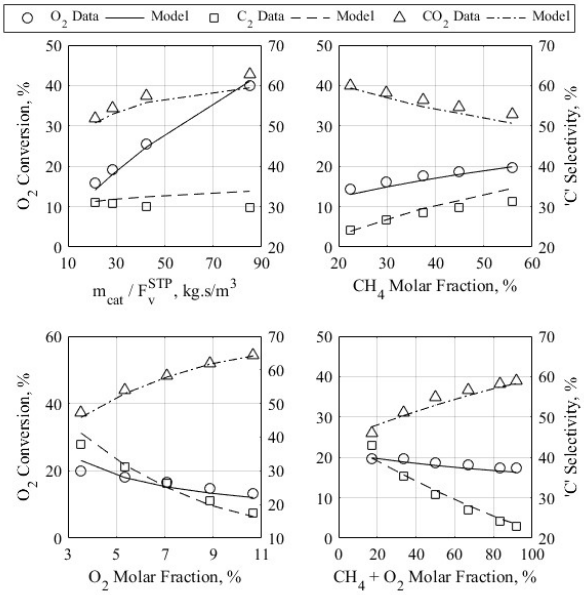

Figure 2. Experimental results and model predictions at 700°C

Table 1. Reaction Scheme

Reactions
$2\ CH_4 + 0.5\ O_2 \rightarrow C_2H_6 + H_2O$
$CH_4 + 1.5\ O_2 \rightarrow CO_2 + H_2 + H_2O$
$CH_4 + O_2 \rightarrow CO + H_2 + H_2O$
$CO + 0.5\ O_2 \rightarrow CO_2$
$C_2H_6 + 0.5\ O_2 \rightarrow C_2H_4 + H_2O$
$C_2H_4 + 2\ O_2 \rightarrow 2\ CO + 2\ H_2O$
$CO + H_2O \leftrightarrow CO_2 + H_2$

Conclusion

Utilizing a fluidized sand bath, we conducted kinetic experiments studying the oxidative coupling of methane over a Sr-Ce-Yb-O catalyst, without mass and heat transfer complications. Based on the experimental data, we proposed a global kinetic model, which shows good agreement with the measurements. This intrinsic kinetic model can be combined with a physical model to help guide the design and operation of an OCM reactor.

References

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