



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Partial oxidation of methane over a ruthenium phthalocyanine catalyst



Yuan Zhu, Robert Barat*

Otto York Department of Chemical, Biological, and Pharmaceutical Engineering, New Jersey Institute of Technology, Newark, NJ 07102 USA

HIGHLIGHTS

- Partial oxidation of methane with oxygen over a heterogeneous catalyst.
- Catalyst is ruthenium-coordinated phthalocyanine encapsulated in zeolite-Y.
- Synthesis gas production observed at 523–648 K range; excellent hydrogen content.
- Excellent catalyst durability with little or no carbon deposition.
- Methane conversion global kinetic rate is first-order in each of methane and oxygen.

ARTICLE INFO

Article history:

Received 2 January 2014

Received in revised form

24 March 2014

Accepted 25 April 2014

Available online 4 May 2014

Keywords:

Catalysis

Kinetics

Gases

Zeolites

Methane

Oxygen

ABSTRACT

The partial oxidation of He-diluted CH₄ with O₂ has been studied in a laboratory flow reactor packed with fragmented pellets of zeolite-encaged Ru phthalocyanine catalyst. Gas compositions (CH₄, O₂, CO, CO₂, and H₂) were determined by on-line GC/TCD. Absolute system pressure was maintained at 445 kPa. Most experiments were performed at a constant gas space velocity = 0.717/s. Data were obtained over wide ranges of temperature (523–648 K) and CH₄/O₂ feed molar ratio (0.5–6.5). Observed conversion of CH₄ increased with temperature. Product selectivities of H₂ and CO increased, while that of CO₂ decreased, with increasing temperature and feed CH₄/O₂. Based on data analysis with an integral plug flow packed bed reactor model, the power law kinetic rate for CH₄ conversion was observed to be first order in each of O₂ and CH₄. A non-linear Arrhenius plot of the global rate constants, together with a Mears correlation analysis, suggests that an external mass transfer resistance becomes active above 573 K in this system.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The economic conversion of natural gas to marketable liquids is of growing importance, especially as modern drilling and recovery methods have created plentiful supplies in recent years. Direct conversion of CH₄ to liquids remains chemically challenging. The indirect pathway to liquids via synthesis gas (syngas) produced from the partial oxidation of CH₄ remains the dominant approach to natural gas upgrading.

The ideal global conversion of CH₄ by partial oxidation to syngas produces H₂ and CO at a molar ratio of 2 to 1. In practice, partial oxidation also produces CO₂ and H₂O. Performed catalytically, the goal is the optimization of CO and H₂ yields at lower temperatures.

The catalysts for CH₄ partial oxidation can be classified into two types. The first type is supported noble metals, most commonly Rh, Ru, Pd, Pt, Ir, etc. Horn et al. (2007) showed that CH₄ could

convert into syngas with high CO and H₂ selectivity on Rh and Pt foam catalysts. Tomishige et al. (2004) and Yamagishi et al. (2006) found that Rh/VO₄/SiO₂ and Rh/SiO₂ are excellent catalysts for partial oxidation with activity at temperatures as low as 773 K. Elmasides et al. (2000) observed syngas formation from CH₄ and O₂ over Ru impregnated onto TiO₂. They concluded that H₂ and CO form directly, while CO₂ and H₂O are secondary oxidation products. Tornaiainen et al. (1994) compared the activities of monolith-supported metals. The highest CH₄ conversion, 89%, was achieved on Ru at 1273 K. The activity of Ni was close to Ru, but deactivation occurred.

The second group consists of supported base metal catalysts, including Ni, Co, Fe, etc. Because of their considerable activity, good stability and lower cost, Fe, Co and Ni catalysts were widely studied. Among this series of metals, Ni has the best activation, which is close to Pt. Choudhary et al. (1997a, 1997b) researched activation on NiO catalyst supported by MgO, CaO, Al₂O₃, SiO₂ and rare earth oxides. The results indicated that when supported by CaO, the catalyst could maintain a high efficiency for long reaction time with no carbon deposit. Dissanayake et al. (1991) studied partial oxidation over 25 wt% Ni/Al₂O₃ within 723–1173 K. They

* Corresponding author. Tel.: +1 973 596 5605; fax: +1 973 596 8436.

E-mail address: barat@njit.edu (R. Barat).

found that CH₄ was almost completely converted at temperatures over 973 K, with a CO selectivity above 95%.

In addition to uncoordinated metals, metal ions complexed by ligands are known to derivatize CH₄. Phthalocyanines (Pc) form coordination complexes with many elements, mostly metals, by the formal replacement of two protons in the parent molecule, H₁₆PcH₂. Amongst metal derivatives, Ruthenium Pc has been investigated in a range of catalytic applications (Rawling and McDonagh, 2007).

Chan and Wilson, Jr. (1988), using a zeolite-encased metal-coordinated phthalocyanine and a fixed-bed flow reactor, showed that CH₄ partial oxidation occurs catalytically. Reaction conditions were 648 K, 445 kPa (abs.), feed molar ratio CH₄/O₂=4, and gas space velocity=0.717/s. Compared to Co and Fe phthalocyanines, the Ru complex showed consistent syngas activity, with less metal complex used.

Prompted by the ability of metal-coordinated phthalocyanines to support the oxidation of C–H bonds, Ru phthalocyanine is used in this paper to investigate the oxidation of CH₄ in a packed bed laboratory flow reactor. Methane conversion global kinetics and product selectivities are determined.

2. Experimental

2.1. The catalyst

Ruthenium-coordinated phthalocyanine (H₁₆PcRu) was encapsulated within zeolite-Y by first exchanging zeolite with Ru cations, followed by the reaction with phthalonitrile. To avoid a large pressure drop in the experimental reactor, the fine catalyst powder was first pelletized with a dye and press, then the pellets were chopped into 0.002–0.003 m chunks. Finally, the catalyst chunks were fixed in the center of the reactor tube by glass wool plugs. As a baseline, pellets of pure zeolite were also prepared and tested.

2.2. The apparatus

The experimental apparatus used in this study consists of calibrated mass flow controls and gas delivery; a 0.013 m OD stainless steel reactor tube; a 3-zone controlled electric furnace; and an on-line gas sampling and analysis setup. System pressure is maintained with a back-pressure regulator. The catalyst zone occupies a small region in the center of the steel tube. Thermocouples are axially inserted into the reactor tube, with their tips just upstream and downstream of the catalyst zone.

Gas analysis is performed with a model 5890 Hewlett-Packard gas chromatograph with thermal conductivity detector (GC/TCD). The He carrier gas flow rate is 0.5E–6 standard cubic meters per second (scms) through a packed column held kept at 303 K. The peaks are recorded and quantified using Vernier® Logger-Pro® software.

Two gas standards were used. The first contains CO, CO₂, O₂, and CH₄, each at 1 mol% with balance He; the second contains H₂ (7%) and balance N₂. A 6-port gas sample valve with sample loop is used for injecting a known amount of gas into the GC/TCD. This sample loop is always filled to the same pressure and temperature for both calibration and experimental samples. Analysis of unknowns uses the single-point and zero gas calibration.

2.3. Partial oxidation conditions

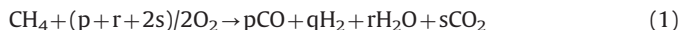
For the partial oxidation experiments, the temperature range studied was 523–648 K, with a CH₄/O₂ feed molar ratio (MR) ranging from 0.5 to 6.5. Most experiments were performed at a

total flow rate of 1.08E–5 scms (~91% He), with a system pressure at 445 kPa (abs.). The catalyst mass was 0.0099 kg, for a gas space velocity of 0.717/s. These conditions are consistent with those of Chan, and Wilson, Jr. (1988). It should be noted that Chan and Wilson, Jr. pretreated their reactor-loaded catalyst with H₂ at a reduced flow rate at 473 K for 3600 s. This pretreatment step was not performed in the current study.

3. Results

3.1. Mole balances

The overall reaction stoichiometry can be taken as follows:



Carbon mole balances were tested on all runs, based on the measured feed CH₄ content, and the measured effluent components CO, CO₂, and unreacted CH₄. Excellent carbon balances were always achieved in this study. For example, at a feed CH₄/O₂ ratio=4.98, inlet CH₄ composition was 6.17%. The observed outlet carbon species compositions were: 0.75% CO₂, 0.32% CO, and 5.07% unreacted CH₄, totaling 6.14%. Such balances also indicate that carbon deposition on the catalyst surface or in its interior was negligible.

No H₂O vapor data were collected in this study. However, an oxygen atom balance is derived since O₂, CO, and CO₂ are accurately measured, and O₂ is the only oxygen atom source in the feed gas. The H₂O content is then estimated by difference.

With the C and O atom balances being complete, the H atom balance is determined. Since H₂O is estimated, and CH₄ measured, the concentration of H₂ is calculated. These estimated H₂ values can be compared to the experimental H₂. An acceptable comparison is a bonus as reliability of the H₂ data is not strong since a linear TCD response for H₂ in a He carrier exists only up to a few mole %. Generally speaking, measured and estimated H₂ contents were reasonably comparable for these low concentrations.

3.2. Stoichiometry

The variable composition of the reactor effluent shows that the overall stoichiometric coefficients in Eq. (1) depend on operating conditions. There is a negligible change of total moles in current system as the feed is highly diluted by He. Therefore, the volumetric flow rate of the total gas is constant through the reactor. The stoichiometric coefficients can be estimated by simply using the inlet and outlet mole fractions (mf).

For example, $p = \text{outlet CO mole fraction} / (\text{inlet CH}_4 \text{ mole fraction} - \text{outlet CH}_4 \text{ mole fraction})$. Similar statements can be made for the other product coefficients q , r , and s .

Fig. 1 illustrates that, at a given temperature, there is generally only limited variability in the CO coefficient with $MR > 1$. As an approximation, the coefficient p can be taken as a function of temperature only, with average values calculated at each temperature. This was also observed for q (H₂) and s (CO₂). These results are presented in Table 1.

Values for the coefficients p , q , r , s , and $(p+r+2s)/2$ were calculated for all runs at a fixed temperature and variable molar feed CH₄/O₂. At a fixed temperature, the coefficients were found to be effectively independent of feed CH₄/O₂. Average values were calculated, and then plotted as functions of temperature. An example for coefficient p is shown in Fig. 2. Table 2 presents the correlations as functions of temperature. Because the stoichiometric coefficients of the overall reaction are not fixed constants, the product coefficients (p , q , r , s) can be considered equivalent to the corresponding product selectivities based on CH₄ conversion.

Download English Version:

<https://daneshyari.com/en/article/6590986>

Download Persian Version:

<https://daneshyari.com/article/6590986>

[Daneshyari.com](https://daneshyari.com)