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C_2 yield enhancement during oxidative coupling of methane in a nonpermselective porous membrane reactor

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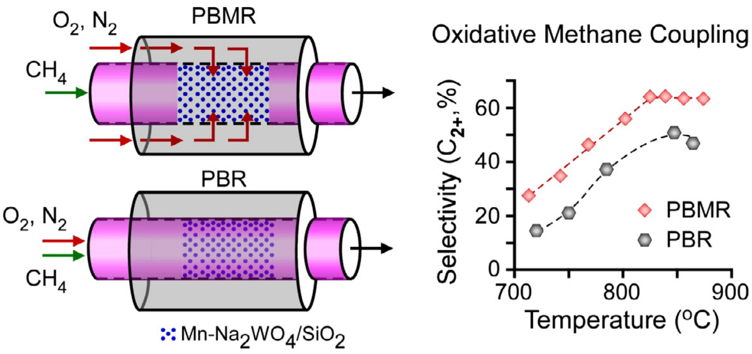
HIGHLIGHTS

- Comparative study done on distributed feed and co-feed policy for OCM.
- Transmembrane pressure adjusted to achieve desired O_2 flux.
- Enhanced C_{2+} yield to 23.6% for PBMR versus 18% for PBR.
- Ways to avoid dilution as transmembrane feed policy are studied.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic comparison between a packed bed membrane reactor (PBMR) and packed bed reactor (PBR) for oxidative coupling of methane (OCM) on Na_2WO_4-Mn/SiO_2 catalyst reveals the utility of distributing the oxygen feed along the catalyst bed length. A sufficiently high transmembrane pressure difference is needed to realize a moderate C_{2+} yield enhancement (~30%). The enhancement is attributed to a shift in selectivity towards the desired coupling reaction by maintaining a high methane to oxygen ratio along the bed length. The elevated transmembrane pressure is achieved by adjusting the shell and tube side parameters including catalyst particle size, inert dilution ratio, residence time, and temperature. Under identical reaction conditions, a C_{2+} yield of 23.6% is obtained for the PBMR compared to 18% for the PBR. The potential detrimental impact of an axial pressure drop in the catalyst bed is compensated by increasing the shell side pressure through an increase in the shell-side nitrogen dilution ratio. Experiments were conducted at lower nitrogen dilution by increasing the catalyst particle size and reducing the tube side pressure. At a dilution ratio of ~38%, a C_{2+} yield of 20% compared to 17% in PBR was obtained, which is on the higher end of the C_{2+} yield reported in literature for a distributed feed membrane reactor at a low dilution. Ways to overcome bypassing of the catalyst bed by shell side O_2 as well as back diffusion of methane were also investigated. The results emphasize the crucial role of transmembrane pressure in enhancing the distribution of oxygen feed along the reactor length for improved OCM catalyst performance.

1. Introduction

The emergence of shale gas production has generated a growing interest in the use of natural gas not only for power generation but also as a chemical feedstock. Since the 1980s efforts to develop

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natural gas as a feedstock has been driven by low natural gas prices relative to petroleum. The largest tonnage petrochemical, ethylene, is a crucial building block for a wide range of chemicals, and has a projected global capacity of 200 million tons per year by 2020 (Eramo, 2013). Most ethylene is produced from the energy intensive steam cracking of natural gas (ethane) and naphtha feedstocks. The oxidative coupling of methane (OCM), first reported by Keller and Bhasin (1982), offers a less energy intensive, single-step conversion of methane to ethylene. To date, methane to ethylene yields have not exceeded ~26% under stable reaction conditions (Ghose et al., 2013). This rather low yield has been an obstacle to OCM commercial feasibility. Moreover, high reaction temperatures of 700–900 °C are required to generate methyl radicals that couple to form C_2 and higher hydrocarbons (Maitra, 1993; Takanabe and Iglesia, 2009). These conditions are unfortunately conducive to the non-selective conversion to carbon oxides and to catalyst deactivation.

Various aspects of the OCM reaction system have been studied, including the underlying mechanism (Jiang et al., 1993; Lunsford, 1995; Takanabe and Iglesia, 2009), influence of catalyst composition (Maitra, 1993; Malekzadeh et al., 2008), reactor design (Coronas et al., 1994b; Wang et al., 2011) and parametric sensitivity (Korf et al., 1990; Schweer et al., 1994; Stansch et al., 1997). Su et al. (2003) presented a case for an upper limit on C_{2+} yield of 28% based on a thermokinetic analysis of a conventional packed bed reactor with continuous feed operation. They suggested that alternate reactor/separation schemes may be the only way to overcome this limit. A number of earlier studies of alternative reactor designs in addition to fixed bed reactor studies (Ghose et al., 2013; Korf et al., 1990; Malekzadeh et al., 2008; Stansch et al., 1997) have included the distributed feed membrane reactor (Bhatia et al., 2009; Coronas et al., 1994b; Sunarso et al., 2008), fluidized bed reactor (Mleczko et al., 1996), and monolith reactor (Wang et al., 2011).

The OCM reaction system has an underlying parallel-consecutive structure represented by

$$\text{Desired reaction}: \quad A + \nu_1 O_2 \rightarrow D \quad r_1 = k_1 C_A^{\alpha 1} C_{O2}^{\beta 1} \tag{1}$$

$$\text{Undesired reaction}: \quad D + \nu_2 O_2 \rightarrow U \quad r_2 = k_2 C_D^{\alpha 2} C_{O2}^{\beta 2} \tag{2}$$

where A represents hydrocarbon reactant, D the desired product, U the undesired product, ν_i the stoichiometric coefficients, k_i the rate constants, C_i the concentrations and α_i, β_i reaction orders. The intermediate product yield in such a parallel-consecutive network may be increased using a membrane reactor if certain features of the kinetics are satisfied (Harold and Lee, 1997). Specifically, for selective oxidation reaction systems if the reaction order with respect to O_2 for the formation of the desired product D is smaller than that for the formation of the undesired product U ($\beta_2 > \beta_1$), a sustained low oxygen concentration can enhance the product selectivity. Modeling studies (Lu et al., 1997; Santamaría et al., 1992) have shown that by sustaining a low oxygen concentration the complete oxidation can be minimized, leading to an enhancement in the intermediate product selectivity.

The packed bed membrane reactor enables controlled distribution of O_2 along the length of the catalyst bed, resulting in a nearly constant, high local hydrocarbon to oxygen ratio. For this reason, distributed feed membrane reactors have found application in selected partial oxidation reactions including oxidative dehydrogenation of alkanes to olefins (Ramos et al., 2000; Téllez et al., 1997; Tonkovich et al., 1996) and methanol to formaldehyde (Diakov et al., 2002).

The two most common type of membranes used in a distributed feed reactor are the permselective dense membrane and non-permselective porous membrane. While dense membranes generally have a higher permselectivity than porous membranes, the permeation flux is low, limiting the reactor productivity (Xu and Thomson, 1997). In contrast, a porous ceramic membrane has potentially much higher flux but its selectivity is lower. In addition, back diffusion of the low pressure side reactant to the higher pressure side and selective permeation of the shell side feed near the back end of catalyst bed have undesirable effects on overall performance. The porous membrane permeability is a key variable in the controlled addition of oxygen into the tube-side methane feed stream. The membrane reactor operation requires that the supply rate of oxygen balances that of the hydrocarbon feed rate to achieve the desired molar feed ratio. In the absence of a sufficient transmembrane pressure gradient, back diffusion of tube side reactant (such as methane in the case of OCM) to the feed side (oxygen stream for OCM) can occur. The membrane morphology plays a major role in achieving the desired transmembrane flux for a prescribed pressure gradient. Papavassiliou et al. (1997) emphasized the significance of transmembrane pressure drop on conversion and reactant/product partitioning between the core and shell side of membrane in porous membrane. Their analyses showed that achieving a prescribed supply flux while minimizing back diffusion requires a unique combination of the pore size and porosity. The permeability and pore size together determine the extent of back diffusion flux of the methane to the shell-side O_2 stream.

Complicating matters is the axial pressure drop in the catalyst bed; a large drop may undermine the achievement of a uniform supply flux due to the resulting transmembrane pressure drop dependence on axial position. In such a scenario the oxygen feed might preferentially be supplied towards the back end of reactor which would tantamount to bypassing. This can lead to reduced contact of the two main reactants and a reduction in their conversion upstream and an over-oxidation downstream.

On comparing generic Eqs. (1) and (2) discussed earlier with OCM, species A represents CH_4, D represents C_2H_4/C_2H_6 and U represents CO_2/CO. Kinetic studies on the OCM reaction over different catalysts (Stansch et al., 1997; Takanabe and Iglesia, 2009) have shown that the reaction order in oxygen for formation of desired reaction products (C_2 hydrocarbons) is lower than the reaction order in oxygen for formation of undesired total oxidation products (CO_2, CO) i.e. $\beta_2 > \beta_1$. Hence, from a kinetic perspective OCM reaction system has attributes that make it a candidate for the distributed feed membrane reactor approach. Although the more complicated OCM reaction network involves a parallel-consecutive reaction, here for comparison purpose we have considered the simpler case of consecutive reaction. The first work reported on OCM in a membrane reactor was by Otsuka et al. (1985) who electrochemically pumped oxygen through a yttria-stabilized zirconia membrane. Membranes with perovskite and fluorite structures offer the advantage of the combination of high ionic and electronic conductivity. In the last decade work has been mainly focused in developing a mixed ionic-electronic conducting membrane material with a high oxygen flux and better thermal and chemical stability as most of these materials undergo a phase change when exposed to CO_2 and water vapor in OCM reaction conditions (Sunarso et al., 2008).

Several studies of OCM have been conducted using different membrane reactor types. Coronas et al. (1994a, 1994b) applied a modified porous α-alumina asymmetric membrane to OCM. The membrane permeability was reduced by depositing silica sol inside the porous alumina structure. Using an asymmetric γ-alumina coated membrane reactor and a diluted oxidant feed, Lu et al. (2000) observed 10% higher C_2 yield and 30% higher C_2 selectivity compared to co-feed reactor at the same methane conversion. Godini et al. (2013) obtained 18% C_{2+} yield at 40% nitrogen dilution in silicon oxycarbide modified alumina membrane packed with Na_2WO_4-Mn/SiO_2 catalyst prepared by wetness impregnation.