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Design and demonstration of an experimental membrane reactor set-up for oxidative coupling of methane

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ABSTRACT

In this experimental research, the performance of the oxidative coupling of methane (OCM) reactions in a porous packed bed membrane reactor was investigated. A commercially available porous alpha-alumina membrane was modified to obtain the characteristics needed for a stable and catalytically inert OCM membrane reactor. The silica-sol impregnation–calcination method and a new silicon oxycarbide (SiOC) coating-calcination approach were applied to modify the membrane. The characteristics of the resulted membrane and its typical performance as OCM membrane reactor are reported.

Generally, it was observed that the combination of these modification methods positively contributes in lowering the undesired activity of the membrane due to simultaneous achieving a small pore-volume structure and a homogeneous modified membrane surface.

Using a flexible experimental set-up, the effects of operating temperature, methane/oxygen ratio, and nitrogen dilution were investigated. The design specifications of this reactor set-up are also reported in details. It was observed that implementing the proposed membrane modification and applying a proper temperature profile significantly improve the oxygen distribution, the selectivity toward the desired products (C_2) and controlling the hot-spot formation. 18.5% C_2-yield and 57% C_2-selectivity were achieved in low diluted gas stream.

Moreover, the performance of the membrane reactor in terms of the selectivity, methane conversion and hot-spot formation was compared with the performance of a fluidized bed reactor. This enables one to analyze the mechanisms through which the operating parameters affect the membrane reactor performance and design an efficient membrane reactor accordingly.

Keywords: Ceramic membrane modification; Packed bed membrane reactor; Oxidative coupling of methane; Flexible experimental set-up; Silicon oxycarbide

1. Introduction

Direct conversion of methane to ethylene via oxidative coupling of methane (OCM) process yet should overcome several operating challenges. Avoiding the hot-spot formation and achieving simultaneous high methane conversion and high ethylene selectivity in the reactor section are among the most challenging tasks. These should be addressed by developing an efficient reactor engineering strategy, which evolves the OCM to become a promising alternative approach for better utilizing the very large available natural gas resources. In so doing, different catalysts and reactor feeding policies have been studied during recent three decades (Mleczko and Baerns, 1995; Zavyalova et al., 2011).

In the co-feeding reactor structures such as fluidized bed reactor and fixed bed reactor (FBR) the practical yield of

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Nomenclature

Symbol and abbreviation Quantity (unit)/full name and definition

C_2	ethane + ethylene
FBR	fixed bed reactor
Methane conversion	portion of the inlet methane converted to the desired and undesired products
OCM	oxidative coupling of methane
PBMR	packed bed membrane reactor
PMS	polymethylsiloxane
R	methane/oxygen ratio
Selectivity	portion of the whole consumed methane which appears in the desired products
T	temperature (degree centigrade °C or K)
UniCat	Unifying Concepts in Catalysis: a research group on catalysis, coordinated by Berlin Institute of Technology and founded by German Research Foundation
Yield	amount of methane appears in the desired product per whole inlet methane

ethylene is limited because of the unselective performance. Moreover, in contrast to the isothermal performance of a fluidized bed reactor, severe hot-spot formation restricts the fixed bed reactor's performance. On the other side, a membrane reactor concept offers a selective performance mainly due to the controlled dosing of the oxygen. Feeding the oxygen into the OCM catalytic bed through discrete feed points (or gradually through a membrane) leads to high local methane/oxygen ratio and ensures a significant selective-methane conversion (Coronas et al., 1994). In comparison to other reactor concepts investigated for OCM application, the use of a membrane reactor can lead to higher selectivity and ethylene yield (Kiatkittipong et al., 2005).

After pioneer experimental research on the application of membrane reactor for OCM (Otsuka et al., 1985), different materials have been tested in the membrane reactor structure for oxygen dosing duty. Some of these researches have exploited the advantage of the dense membrane reactor to selectively supply the oxygen reactant from air (Langguth et al., 1997; Czuprat et al., 2010). Several other researchers have investigated the catalytic membrane reactors for this application to reduce the potential of hot-spot formation and avoid the pressure drop along the catalytic bed (Bhatia et al., 2009).

Considering the advantages and disadvantages of different structures of the membrane reactors so far applied for the OCM application, a porous packed bed membrane reactor (PBMR) with significant diffusion potential per unit area and proper contact time–volume ratio was chosen to be intensively investigated in UniCat.[1]

Vycor glass (Ramachandra et al., 1996) and ceramic membrane (Lafarga et al., 1994) have been used as OCM porous membrane reactor. Usually the available ceramic membranes used for this application are made of alpha-alumina with the pore size bigger than 200 nm, which shows a stable porous structure under the OCM reaction temperature. Since such a membrane does not provide the desired range of the cross-membrane pressure gradient for the required range of oxygen flux, the membrane permeability and thereby the amount of the gradient force for the gas flux across the membrane should be properly modified. In this research, this is achieved via known silica sol impregnation–calcination method (Lafarga et al., 1994) and a novel modification procedure using silicon oxycarbide (SiOC).

This experimental research covers the membrane modification, analyzing the performance of the resulted PBMR and comparing its observed performance with the performance of a FBR and fluidized bed reactor. In this context, the effects of operating parameters such as temperature, pressure gradient, methane/oxygen ratio and nitrogen dilution will be experimentally investigated. All these reactor set-ups have been constructed in the UniCat mini-plant along with the OCM downstream separation units (Stünkel et al., 2011) in order to investigate the whole OCM process via concurrent engineering approach.

2. Experimentations

In the first part of this section, the membrane modification methods are described. Then, the experimental set-up used for studying the performance of the resulted modified membranes under various operating conditions is described.

2.1. *Membrane modification*

The commercial micro-filtration ceramic membranes used as the OCM membrane reactor normally have one supporting layer to assure the mechanical strength and a membrane layer to do the main separation duty. The support layer is made of alpha-alumina with the micrometer pore size, which is structurally stable under the OCM operating temperature. On the other side, a thin membrane layer with very small pore size is needed for fine dosing of oxygen and providing a sharp radial partial pressure gradient for the components across the membrane tube. Such membrane layer should be also structurally stable under the OCM reaction temperature. The available ceramic membranes in market cannot fulfill both of these permeability and stability requirements simultaneously. Therefore, a stable alpha-alumina membrane layer with the nominal pore size of 200 nm was modified to obtain the required permeability characteristics via two modification procedures.

2.1.1. *Material and methods for membrane modification*

The 600 mm long micro-filtration membranes with the initial characteristics reported in Table 1 were supplied by Fraunhofer institute. The cross sectional SEM picture and the result of mercury porosimetry test over the fresh membrane are shown in Fig. 1 confirming the nominal specifications.

Concentration of oxygen inside the membrane porous structure (Al_2O_3 support layer) is higher than inside the catalytic bed. On the other side, methane can also diffuse back into this area. Therefore, it was expected and observed that the big pores in this porous structure contribute to the gas phase reactions mostly in favor of the combustion reactions. This results in an unselective conversion. In order to reduce the size of the pores mainly in the support layer, the silica-sol impregnation–calcination method was applied. This method has been specifically suggested for developing an OCM

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