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ScienceDirect
Journal of Natural Gas Chemistry 21(2012)534–543
Journal of Natural Gas Chemistry
www.elsevier.com/locate/jngc

Experimental investigation of fluidized-bed reactor performance for oxidative coupling of methane

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[Manuscript received February 20, 2012; revised July 4, 2012]

Abstract

Performance of the oxidative coupling of methane in fluidized-bed reactor was experimentally investigated using Mn-Na_2WO_4/SiO_2, La_2O_3/CaO and La_2O_3-SrO/CaO catalysts. These catalysts were found to be stable, especially Mn-Na_2WO_4/SiO_2 catalyst. The effect of sodium content of this catalyst was analyzed and the challenge of catalyst agglomeration was addressed using proper catalyst composition of 2%Mn-2.2%Na_2WO_4/SiO_2. For other two catalysts, the effect of Lanthanum-Strontium content was analyzed and 10%La_2O_3-20%SrO/CaO catalyst was found to provide higher ethylene yield than La_2O_3/CaO catalyst. Furthermore, the effect of operating parameters such as temperature and methane to oxygen ratio were also reviewed. The highest ethylene and ethane (C_2) yield was achieved with the lowest methane to oxygen ratio around 2. 40.5% selectivity to ethylene and ethane and 41% methane conversion were achieved over La_2O_3-SrO/CaO catalyst while over Mn-Na_2WO_4/SiO_2 catalyst, 40% and 48% were recorded, respectively. Moreover, the consecutive effects of nitrogen dilution, ethylene to ethane production ratio and other performance indicators on the down-stream process units were qualitatively discussed and Mn-Na_2WO_4/SiO_2 catalyst showed a better performance in the reactor and process scale analysis.

Key words

oxidative coupling of methane (OCM); fluidized-bed reactor; catalyst stability

1. Introduction

After the intensive research period in the 1980's and 1990's on oxidative coupling of methane (OCM), this topic is again attracting attention. Using this process, the huge resource of natural gas can be upgraded to high demand chemical intermediates. This process consists of three main subsections namely reaction section, CO_2 removal section and ethylene separation and purification section [1]. The interconnections between these sections are shown in Figure 1.

In the reaction section, methane reacts with oxygen, in order to produce ethylene. Table 1 shows the set of OCM reactions which has been widely referred as a straightforward representation of OCM kinetic [2,3]. This reaction set includes the main desired coupling and undesired combustion reactions. This set consists of nine surface reactions and one gas phase reaction. However, in order to fully cover other crucial gas phase reactions, the reactions reported by Lane et al. [4] have been also reported in this Table.

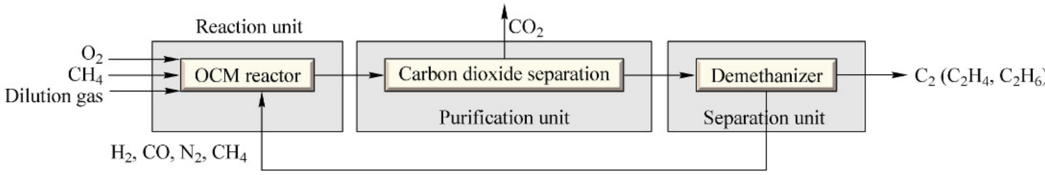

Figure 1. Block-flow diagram for oxidative coupling of methane (OCM) process

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This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

doi:10.1016/S1003-9953(11)60402-7

Table 1. Surface and gas phase reactions involved in OCM reaction network

Surface reaction	Gas reaction [4]
(1) $CH_4+2O_2 \rightarrow CO_2+2H_2O$	(1) $CH_4+2O_2 \rightarrow CO_2+2H_2O$
(2) $2CH_4+0.5O_2 \rightarrow C_2H_6+H_2O$	(2) $CH_4+1.5O_2 \rightarrow CO+2H_2O$
(3) $CH_4+2O_2 \rightarrow CO+H_2O+H_2$	(3) $2CH_4+0.5O_2 \rightarrow C_2H_6+H_2O$
(4) $CH_4+0.5O_2 \rightarrow CO_2$	(4) $2CH_4+O_2 \rightarrow C_2H_4+2H_2O$
(5) $C_2H_6+0.5O_2 \rightarrow C_2H_4+H_2O$	
(6) $C_2H_4+2O_2 \rightarrow 2CO+2H_2O$	
(7) $C_2H_6 \rightarrow C_2H_4+H_2$	
(8) $C_2H_4+2H_2O \rightarrow 2CO+4H_2$	
(9) $CO+H_2O \rightarrow CO_2+H_2$	
(10) $CO_2+H_2 \rightarrow CO+H_2O$	

La_2O_3/CaO catalyst is from Ref. [2]; $Mn/Na_2WO_4/SiO_2$ catalyst is from Ref. [3]

So far different reactor concepts and feeding policies have been tested to increase the yield of the desired reactions. In an efficient OCM reactor, several parameters have to be exploited properly and the operating limitations should be taken into consideration, so that the undesired CO_2 production is reduced and higher amounts of ethylene and ethane (C_2 products) can be achieved. However, the effect of these parameters is not limited to the reactor section and should be evaluated in the context of the whole process performance.

Recent achievements on developing efficient catalysts and robust large scale catalyst preparation methods [5] along with developing new alternative material and methods to be used in the reactor and separation sections, have motivated many researches to re-analyze OCM potential in the light of these new aspects. An efficient way to exploit all these factors for improving OCM process design is to follow a concurrent engineering path. The design driven factors in a concurrent engineering approach are the effect of each local parameter (parameter in each section) on the whole process performance. Such an approach has been applied in the mini-plant scale experimental facility for OCM process in Berlin Institute of Technology as a part of UniCat* research program. Via this approach, several alternatives in different sections of OCM process are simultaneously analyzed. In the reactor section of UniCat OCM project, fixed-bed reactor, membrane reactor and a fluidized-bed reactor were analyzed experimentally.

In this paper we report the experimental performance of a fluidized-bed reactor for three OCM catalysts and conceptually interpret their performance not only according to the reactor engineering aspect but also in the wider context of the whole OCM process performance evaluation.

Fluidized-bed reactor was selected because of its capability to efficiently address one of the most serious operating challenges of OCM reactions, i.e., the huge release of heat due to the exothermic reaction, which can cause forming hot spots in the reaction zone. This has motivated several researchers to investigate OCM reactions in fluidized-bed reactor [6–8].

2. OCM catalyst selection

Various metal oxides have been investigated to serve as OCM catalysts. Table 2 reveals the specifications and performance of three types of catalysts, which have been tested so far in fluidized-bed reactor and have shown considerable amount of C_2 production yield. Detailed review can be found elsewhere [8].

Although the lithium-based catalysts are among the most studied OCM catalysts, but they have shown a poor stability [12,13]. Stability of the catalyst is a very important aspect and essential requirement for its possible industrial application. Lanthanum oxide catalyst and $Mn-Na_2WO_4/SiO_2$ catalyst have also been used in the experimental investigations and shown a stable behavior.

Table 2. Selected reported results on the performance of different catalysts in fluidized-bed reactor

Catalyst precursor and promoters type	Na-promoted Sr-catalyst	(La/Sr/Zr) catalyst	(Li/Sn/MgO) catalyst
Operating conditions	T = 850 °C	T = 880 °C, CH_4/O_2 = 2.5	T = 800 °C, CH_4/O_2 = 2
The observed performance	C_2-Sel. of 77%, CH_4 conv. of 28%*	C_2-Sel. of 50%, CH_4 conv. of 36%*	C_2-Sel. of 48%, CH_4 conv. of 45%*
Concern and consideration	highest yield obtained in relatively low methane conversion	–	not a stable catalyst
Reference	Do et al. 1995 [9]	Mleczko et al. 1996 [10]	Santos et al. 1997 [11]

* CH_4 conv.: methane conversion; C_2-Sel.: ethylene and ethane selectivity

Lanthanum-based catalysts clearly have shown a good potential to be used in laboratory scale (5−7 cm diameter) and industrial scale (4 m diameter) fluidized-bed reactors [7]. $Mn-Na_2WO_4/SiO_2$ catalyst has been tested in other type reactors and has also shown a promising performance [14]. The performance of these catalysts in a fluidized-bed reactor will be investigated in the next sections of this paper in regard to operability, yield and selectivity.

2.1. Na-W-Mn catalytic system

$Mn-Na_2WO_4/SiO_2$ catalyst is known to be one of the most selective and stable catalysts developed for OCM process. This tri-metallic catalyst prepared in this research was in the form of $2\%Mn-4.5\%Na_2WO_4/SiO_2$ since Fang et al. [15] originally reported a highly active and selective performance for similar composition. However, this composition may need to be optimized in terms of amount of metallic species in order to provide a sustainable performance and operability.

For instance, Ji et al. [16] varied the composition of the alkali promoter as well as the promoter itself, and they observed that sodium is able to create a stable structure over the support surface and simultaneously increase methane conversion and selectivity toward ethylene. However, this might cause operational problems. For further analyzing the potential of Mn-