



Sol–gel method for synthesis of Mn–Na₂WO₄/SiO₂ catalyst for methane oxidative coupling



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ABSTRACT

In this experimental study, a novel sol–gel method was developed to synthesize a 1.9Mn–5%Na₂WO₄/SiO₂ catalyst for oxidative coupling of methane (OCM) reactions. The performance of the synthesized catalyst was investigated in fixed-bed and porous packed-bed membrane reactors. Particularly, the effects of operating temperature, methane-to-oxygen ratio and nitrogen dilution on the performance of this catalyst were investigated. It was observed that for high values of methane conversion, the sol–gel Mn–Na₂WO₄/SiO₂ catalyst provides 5–15% higher selectivity toward the desired products (C₂: C₂H₄ + C₂H₆) than the Mn–Na₂WO₄/SiO₂ catalyst prepared by the incipient wetness impregnation method. It was also observed that for a similar set of experiments, the C₂-selectivity of the sol–gel catalyst is affected relatively less by the variation of methane-to-oxygen ratio. As a result, this catalyst can be exploited under the low methane-to-oxygen feed ratio which provides an efficient performance in both the OCM reactor and the OCM process scale. The best observed performance of the sol–gel catalyst in the packed-bed membrane reactor is 78% C₂-selectivity, 64% ethylene-selectivity and 24.2% C₂-yield under 20% nitrogen dilution.

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1. Introduction

Development of an efficient catalyst for oxidative coupling of methane (OCM) remains to be the most challenging and crucial step in the commercialization of this process. The performance of the OCM catalyst not only affects the efficiency of the down-streaming unit operations in the OCM process but also dictates the thermal-reaction characteristics of the OCM reactor. In the last three decades several catalysts and reactor concepts have been proposed for oxidative coupling of methane (OCM) [1–3]. However, most of these catalysts are either not stable enough for the expected long-term operation on an industrial scale or do not provide a simultaneous high ethylene yield and selectivity. A review over the research activities on OCM catalyst and OCM reaction engineering has been presented in some recent references [4]. Among the investigated

effective OCM catalysts so far, the Mn–Na₂WO₄/SiO₂ catalyst is one of the most stable and recommended catalysts [2,5]. The mechanistic aspects of the OCM over this catalyst and the detailed analysis of interaction of catalyst with the gaseous species have been investigated as the key information required for efficiently exploiting this catalyst in a proper reactor feeding policy [6]. This catalyst can be implemented in an appropriate reactor concept such as a membrane reactor and therefore a selective stable OCM performance can be accomplished using a packed-bed or a catalytic membrane reactor. Catalytic membrane reactor not only offers a fine oxygen feeding policy but it also addresses the exothermicity of this reaction and the concern regarding hot-spot formation. However, an efficient applicable method for implementing the catalyst over the membrane structure should be developed based on the comprehensive understanding of the material and reaction engineering of the system. Being able to provide a homogeneous activated structure with the desired diffusion and surface characteristics are the main criteria for choosing the suitable method for this task.

In this work, a sol–gel synthesis procedure was developed for preparing the Mn–Na₂WO₄/SiO₂ catalyst and catalytic solution which provides the desired characteristics for coating it over the porous structure such as ceramic membrane. The distinguishing

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Nomenclature

BOTZ	commercial glassy material used for coating the ceramics
C ₂	ethane + ethylene
ICP	inductively coupled plasma
ID/OD	inside/outside diameter
IWI	incipient wetness impregnation
FBR	fixed bed reactor
Methane conversion	portion of the inlet methane converted to the desired and undesired products
OCM	oxidative coupling of methane
Selectivity	portion of the whole consumed methane which appears in the desired products
STP	standard temperature and pressure (298 K and 1 bar)
TEOS	tetraethyl orthosilicate
UniCat	“Unifying Concepts in Catalysis”: research group in Berlin
Yield	portion of the inlet methane which appears in the desired products
ρ	catalyst density (kg/m ³)

feature of synthesizing the Mn–Na₂WO₄/SiO₂ with a sol–gel method is that the precipitation of the catalytic precursors does not occur before it is coated over the membrane surface.

In this research, a novel procedure for preparing the sol–gel form of Mn–Na₂WO₄/SiO₂ was developed. The resultant sol–gel was then calcined to prepare the catalytic material in order to test its activity and selectivity in the fixed-bed and packed-bed membrane reactors. Moreover, the performance and characteristics of the sol–gel catalyst were compared with those observed for the Mn–Na₂WO₄/SiO₂ catalyst prepared by a wetness impregnation method. In this context, the effects of operating parameters such as temperature, methane-to-oxygen ratio and nitrogen dilution were comprehensively investigated.

2. Review of Mn–Na₂WO₄/SiO₂ catalyst

The application of Mn–Na₂WO₄/SiO₂ catalyst as an efficient OCM catalyst has been investigated since 1992 [7] and its promising potential for long-term operation has been highlighted since then by several researchers [5,8,9]. This catalyst has been introduced as one of the most stable catalysts for OCM [5,8–10]. Some fundamental and practical researchers have been conducted to further improve the stability of this catalyst and evaluate its operating aspects in different scales [11,12]. Our research group UniCat² has also been very active in analyzing different aspects of this catalyst, from a fundamental understanding of the mechanisms on the catalyst surface to large-scale preparation and testing of the catalyst in a mini-plant scale fluidized bed reactor [9,10,13].

In the context of phenomenological analysis of this catalyst, Ji et al. have contributed significantly to achieve the current understanding of the role of active sites on improving the C₂-selectivity and yield [14–16]. It has been explained that Tungstate stabilizes sodium on the catalyst surface and sodium facilitates the transformation of amorphous silica to α -cristobalite [17,18]. Therefore, it has been reported repeatedly that Na₂WO₄ and WO₄ (tetrahedron) have a crucial role in the selective conversion of methane

[9,19]. The specific role of the α -cristobalite phase on improving the C₂-selectivity has been highlighted and comprehensively investigated in the context of the interaction between the support structure and the cations [8,10,18–21].

It has been reported by several researchers [5,20,22] that using the specific composition of 1.9–2% Mn and 5% Na₂WO₄/SiO₂ for this catalyst will lead to the best performance in terms of the C₂-selectivity and yield. The preparation method also has a crucial impact on the performance of the resulting catalyst. It has been observed that micro-pores are formed on the catalyst structure when W and Na are implemented simultaneously [21]. This is an important aspect since the preparation methods investigated in this research – the wetness impregnation and sol–gel methods – provide different characteristics in terms of the interaction of silica and cations. Wang et al. have tested three preparation procedures which have resulted in three different levels of C₂-yield as reported in Table 1 [22].

In Table 1, the reported performance of the 1.9–2%Mn–5%Na₂WO₄/SiO₂ catalyst produced via various preparation methods and tested in various reactors are reviewed. These data have been obtained under different sets of operating conditions such as gas dilution (%), GHSV (h⁻¹), which have also been reported in Table 1. More information about the set of experimental conditions employed for each case is available in the original references cited in this table.

As seen in Table 1, most of the researches so far have focused on preparing the Mn–Na₂WO₄/SiO₂ catalyst using the wetness impregnation method. Only a few reports are available in which the Mn–Na₂WO₄/SiO₂ catalyst has been prepared using a kind of sol–gel method. In the approaches so far applied for sol–gel preparation of this catalyst, the same metal precursors as in the wetness impregnation method have been used. These metal precursors are mixed with tetraethyl orthosilicate (TEOS) as the source of silica. During the catalyst synthesis via such an approach, an interaction between the Mn(NO₃)₂ and the Na₂WO₄ is likely to be the dominant phenomenon and precipitation is usually faster than the complete establishment of the expected condensation reactions. Therefore, establishing a homogeneous catalyst with uniformly distributed species on the sol–gel network cannot be guaranteed. Moreover, homogeneous coating a porous ceramic support such as an alumina membrane with the catalytic solution prepared by such a preparation procedure is usually not feasible. The microstructure of the prepared catalyst by this method is strongly affected by different parameters such as the type of precursors, the solvent, the drying process, and the calcination temperature. The drying process is typically accompanied by densification. This is a critical step that strongly affects the structure and the characteristics of the final product (pore size distribution, porosity, surface area).

In order to achieve a homogeneous active surface, the source and the procedure of implementing the metal precursors has to be selected carefully. This is the main goal of the current research and it has been accomplished via developing a novel route for synthesizing this catalyst. In order to highlight the specifications of the proposed sol–gel method, the preparation procedure and characteristics of this method and the wetness impregnation method are reviewed first. Then, the performance of the resulting catalysts, prepared by each of these methods, is analyzed in the fixed-bed and membrane reactors and finally compared to each other.

3. Materials and methods

In this section, the wetness impregnation method and the sol–gel method applied for preparation of the Mn–Na₂WO₄/SiO₂ catalysts are described in detail. The characterizations of the resulting catalysts as well as their typical performances are reported in the next sections.

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