



Oxidative coupling of methane using catalysts synthesized by solution combustion method: Catalyst optimization and kinetic studies



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ABSTRACT

The $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst has shown promise for oxidative coupling of methane (OCM). Our prior work demonstrates that $10\%\text{Na}_2\text{WO}_4\text{-5\%Mn/SiO}_2$ prepared by solution combustion synthesis (SCS) exhibits good performance in terms of C_2 yield and ethylene to ethane ratio. In this work, we use SCS for preparation of several modified $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalysts for OCM. The catalyst composition was optimized by addition of different metals and Si precursor used. The optimized catalyst ($5\%\text{La-10\%Na}_2\text{WO}_4\text{-5\%Mn/SiO}_2$, using tetraethoxysilane as the Si precursor) showed the best performance for OCM, with C_2 yield 27% and ethylene/ethane ratio 3.6 under optimized operating conditions, both values are among the highest reported in the literature. Kinetic studies for this catalyst indicated that methane conversion was first-order in methane and half-order in oxygen, implying that methane activation is likely to be rate-limiting and oxygen adsorption is dissociative. The formation rates of primary products (C_2H_6 , CO and CO_2) could be well described by the reaction scheme proposed in a prior work.

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1. Introduction

Methane is the main constituent of natural gas (typically >95%) [1]. In recent years, decrease in natural gas price has spurred research on adding value to this abundant resource. In this context, oxidative coupling of methane (OCM) is attractive for conversion of natural gas into more useful higher hydrocarbons, especially ethylene and ethane. A combined C_2 yield of at least 25% is required for this reaction to be a potentially attractive commercial route [2,3]. Since the original work by Keller and Bhasin [4], numerous metal oxide catalysts have been studied for OCM. These include basic oxides (especially early members of the lanthanide series), alkali and alkaline earth metals supported on basic oxides, monophasic mixed oxides, transition metal oxides (often in combination with alkali metals), and other simple and complex multimetallic oxides [2,3]. A multimetallic oxide of the form $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ has been identified among the highest performing catalysts for this reaction, and has been conventionally prepared using incipient wetness impregnation [5–9].

Solution combustion synthesis (SCS) is a powerful technique for preparation of simple and complex metal oxides. It is related to the sol–gel route [10] and combustion synthesis [11], and involves a self sustained reaction between oxidizers (typically metal nitrates

and fuel (e.g. glycine, hydrazine, etc.) [12,13]. While metal nitrates are the precursors for the metals in the final product, the fuel provides energy, and also acts as a complexing agent in many cases. This method has certain advantages over conventional techniques and has been used for synthesis of several complex multimetallic oxides, for different applications including complex metal oxide oxygen carriers for chemical looping combustion [14], as autothermal JP-8 fuel reforming catalysts [15], anode catalysts in methanol fuel cells [16], oxygen permeating membranes [17], synthesis of perovskite red phosphors [18], preparation of iron oxides for varied uses [19], NO_x decomposition catalysts [20] and combinatorial materials synthesis [21]. Recently, it has also been used for preparation of highly superacidic sulfated zirconia catalyst for Pechman condensation [22]. Our previous work on OCM involved synthesis of various SCS catalysts, among which $10\%\text{Na}_2\text{WO}_4\text{-5\%Mn/SiO}_2$ was the most promising and showed a high C_2 yield of 24%, with ethylene/ethane ratio ~ 2 [23]. Thus, in this work, we investigate variations of this catalyst in an attempt to increase the OCM performance further.

The present study involves optimization of this catalyst by varying certain synthesis parameters and operating conditions. For optimization of catalyst composition, effects of addition of different metals and alternative silica precursors were studied. Further, temperature and flow ratios of methane and oxygen were also varied to determine the optimum operating conditions.

The kinetics of OCM have been intensively studied, and various reaction schemes have been proposed [24–30]. No consensus

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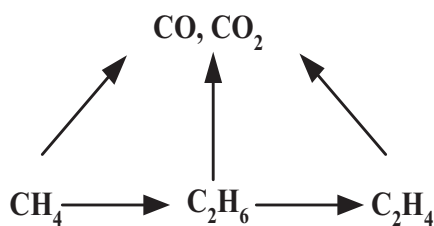


Fig. 1. The simplified reaction network for OCM.

exists, however, even for similar catalysts studied in the literature. A general reaction framework is accepted, according to which the OCM reaction consists of 3 main steps: (a) Activation of methane heterogeneously leading to formation of methyl radicals, (b) coupling of methyl radicals to form ethane, and (c) dehydrogenation of ethane to form ethylene. CO_x (CO and CO_2) may be formed homogeneously or heterogeneously in primary or secondary reaction steps, according to the simplified reaction network (Fig. 1). While the general framework is widely accepted, several different reaction schemes have been derived within this framework for various catalysts, and debate exists concerning the active oxygen species involved in methane activation [2].

The current work also describes kinetic studies on the optimized catalyst using a fixed-bed reactor under differential conversion and anhydrous conditions. The purpose of the kinetic study is to identify a reaction mechanism for the optimum catalyst from among the numerous mechanisms described in the literature.

2. Experimental techniques

2.1. Materials

The specifications of chemicals used are as follows: lanthanum(III) nitrate hexahydrate (Alfa-Aesar, 99.9% pure), sodium tungsten oxide dehydrate (Alfa-Aesar, ACS, >99% pure), nitric acid (Alfa-Aesar, 2.0N), manganese(II) nitrate tetrahydrate (Alfa-Aesar, 98% pure), glycine (Alfa-Aesar, >99% pure), tetraethoxysilane (Alfa-Aesar, >99% pure), aminopropylsilsequioxane oligomer (Gelest Inc.), dimethylsiloxane-ethyl oxide block copolymer (Gelest Inc.) and silica (Sigma-Aldrich, Davisil grade).

2.2. Catalyst synthesis

The SCS was used for preparation of all the studied catalysts in this work. In summary, in this method metal nitrates (in stoichiometric proportions) and fuel are dissolved in deionized water, and heated until most of the water evaporates, leading to spontaneous combustion and formation of desired metal oxide powders. Typically, combustion may occur in two different modes, viz, volume combustion mode (VCS), which is characterized by a sudden uniform temperature rise to maximum temperature T_{max} , or the self-propagating high temperature synthesis (SHS), in which the reaction is initiated at a specific hot spot followed by steady wave propagation along the mixture [11]. Fig. 2 depicts a typical temperature–time profile for 5%La–10% Na_2WO_4 –5%Mn/ SiO_2 catalyst using aminopropylsilsequioxane oligomer as a silica precursor, obtained using a 250 μm K-type thermocouple. The reactants were dissolved in sufficient deionized warm water in a glass beaker, and heated on a hotplate. As the mixture reached the boiling point, the next stage ($4 \text{ min} \leq t \leq 40 \text{ min}$) was characterized by a constant temperature period during which most free and partially bound water evaporated, resulting in formation of a paste-like structure.

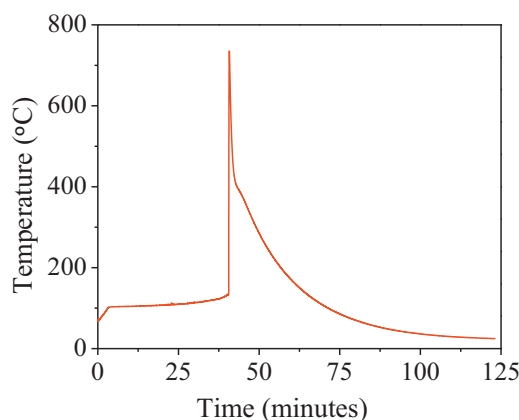


Fig. 2. Typical temperature–time profile during solution combustion synthesis for 5%La–10% Na_2WO_4 –5%Mn/ SiO_2 (Si precursor: aminopropylsilsequioxane oligomer).

This was followed by spontaneous combustion, leading to a uniform temperature rise to maximum value T_{max} of 750 °C in the VCS mode ($t \sim 40 \text{ min}$). Finally, uniform cooling of the fine powders formed was observed ($t > 40 \text{ min}$). A metallic mesh (140 μm opening) was used to cover the beaker to prevent the formed powders from escaping.

As described in our previous work [23], the 10% Na_2WO_4 –5%Mn/ SiO_2 was prepared using Na_2WO_4 and $\text{Mn}(\text{NO}_3)_2$ as precursors for Na, W and Mn, respectively, while tetraethoxysilane (denoted as S1) was used as the silica precursor in this catalyst (NWMS1). Tetraethoxysilane also served as a fuel, and a fuel/oxidizer ratio, $\varphi = 2$ was achieved by adding appropriate amounts of HNO_3 . In the present work, variations of this catalyst with addition of different metals (5%La, 5%Ce and a combination of 5%La with 5%Ce) were studied. These catalysts are referred to as 5%La–NWMS1, 5%Ce–NWMS1, and 5%La–5%Ce–NWMS1, respectively.

Two alternative Si precursors were used for preparation of 5%La–10% Na_2WO_4 –5%Mn/ SiO_2 , viz. aminopropylsilsequioxane oligomer (S2), and dimethylsiloxane-ethyl oxide block copolymer (S3). For these catalysts, referred to as 5%La–NWMS2 and 5%La–NWMS3, glycine was used as an additional fuel. All catalysts described above were synthesized at $\varphi = 2$, and were calcined in air at 950 °C for 4 h. Fig. 3(a) and (b) shows the scanning electron microscope (SEM) images of the as-synthesized and calcined 5%La–NWMS2 catalyst, respectively. It may be seen that the as-synthesized powder is in the form of thin flakes, while the calcined sample is sintered and has a more rounded appearance with particles of about 10 μm characteristic dimension. These results are typical of materials prepared by the solution combustion technique. The performance of all SCS catalysts was tested in a fixed-bed reactor, and the optimum catalyst exhibiting the highest C_2 yield was selected for further kinetic studies.

2.3. Catalyst performance measurements

The catalyst performance measurement experiments were conducted in a modified quartz fixed-bed reactor setup, with separated feed for methane and oxygen, which has been described elsewhere [23]. The typical standard operating conditions were: catalyst weight: 1 g, catalyst size: 125–250 μm , total flow = 50 ml/min, and feed ratio $\text{CH}_4:\text{O}_2:\text{N}_2 = 32:8:10$. The metrics used for catalyst performance were the C_2 yield and ethylene/ethane ratio. The effect of variation of CH_4/O_2 feed ratio was also investigated for each catalyst at its optimum temperature ($\text{CH}_4 = 32 \text{ ml/min}$ and $\text{N}_2 = 10 \text{ ml/min}$).

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