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Research Paper

Oxidative coupling of methane over Mn-Na$_2$WO$_4$ catalyst supported by monolithic SiO$_2$

Cagla Uzunoglu, Aybuke Leba, Ramazan Yildirim*

Department of Chemical Engineering, Boğaziçi University, 34342, Bebek, Istanbul, Turkey

A B S T R A C T

In this work, oxidative coupling of methane was studied over monolithic Mn/Na$_2$WO$_4$/SiO$_2$ catalysts. The monolithic catalysts were prepared by three different ways as (1) preparation of monolithic silica (monosil) followed by impregnation of Mn and Na$_2$WO$_4$, (2) preparation of monolithic silica with Mn addition during gelation (Mn-monosil) followed by impregnation of Na$_2$WO$_4$ and (3) preparation of monolithic silica as MCM-41 structure (MCM-monosil) followed by impregnation of Mn and Na$_2$WO$_4$. The catalysts were tested in a microflow reactor and the results were compared with those obtained over particulate catalysts. It was found that Mn-monosil performed best and produced C$_2$ yield of 16.2%, which is close to the values obtained over particulate catalyst (19.3%). Mn-monosil was also passed the 10 h stability and hysteresis tests successfully. SEM characterization revealed that monolithic catalysts prepared by three different methods had different pore structure; it was also seen from SEM images that Mn-monosil preserved its original form better, and this was also verified by XRD analysis.

1. Introduction

Oxidative coupling of methane (OCM) provides a direct route for ethylene and ethane production from natural gas; CO and CO$_2$ are also produced as undesired by-products [1]. Although OCM has been studied as one of the potentially suitable process to utilize natural gas, there is a major obstacle preventing its commercialization: the desired C$_2$ products (ethylene and ethane) are more reactive than methane at temperatures high enough for significant CH$_4$ conversion [1,2]. Hence either conversion or selectivity toward C$_2$ products is low resulting always low C$_2$ yields. However, the researchers have been still working to overcome this problem for last three decades considering the attractiveness of the process; those works involves testing various catalyst formulations as well as finding optimum reactor configuration and operational conditions to improve C$_2$ yield [3–5].

Various catalysts have been investigated for OCM process to enhance the C$_2$ selectivity and yield; among them, Mn/Na$_2$WO$_4$/SiO$_2$ was found as one of the most effective catalyst [6–11]. It is believed that each element (Mn, Na and W) in the catalyst has a special role, and interaction among them provide the formation of the active centers on the surface of the support. Manganese acts as an oxygen supplier for tungsten due to its high electronic conductivity and increase the stability of the catalyst; sodium, which acts as a structural promoter, has a dual role to produce desired products as well as to inhibit by-products.

Tungstate, on the other hand, provides the formation of active sites through both W=O and W−O−Si groups [10–12]. Several researchers have studied various compositions of catalyst in order to obtain the optimum performance [6,7,9,13–15]; it generally suggested that the composition should be around 2% Mn and 5% Na$_2$WO$_4$ for maximum yield. The replacement of the elements in Mn/Na$_2$WO$_4$/SiO$_2$ with other alternatives has not been produced any improvement verifying that the combination of manganese, sodium and tungsten in the ratios mentioned above is required for high performance [7,11,16].

It is observed, at various studies that, the temperature in the range of 600–800 °C is needed to break the C−H bonds in methane and to reach significant conversion. However, higher temperature also causes the catalyst deactivation and the formation of by-products. This problem is worsening by the difficulties in temperature control of the catalyst bed; the studies have shown that there were about 150 °C temperature difference between the catalytic bed and the reactor furnace [17].

Desirable yields strongly depend on the feed composition as well; finding the optimum feed composition is crucial to minimize the gas phase reactions leading undesired by-products [18,19]. The oxygen concentration in the feed is vital; a higher concentration lead to an increment of the side reactions while too low O$_2$ concentration causes low CH$_4$ conversion [6,11].

The physical structure of Mn/Na$_2$WO$_4$/SiO$_2$ catalyst also seems to

play an important role in OCM reactions. It is believed that the reaction proceeds through the formation of CH_3 radicals on the catalyst surface followed by their combination in gas phase [20,21]; this may be indicating that some empty space around the catalytic material is required. However, undesired CO_x species are also formed in the gas phase as it is evident from the fact that filing the empty space before and after the catalyst bed with quartz chips improves the C_2 yield [9,17,23]. As the results, there should be an optimum void structure to have desired C_2 yield, and even a successful particulate catalyst worked well in the laboratory may not do so in industrial applications because the void structure will be completely changed in scale up process. Hence, using a catalyst (like monoliths), of which the void structure can be preserved during scale up process, may be beneficial for the commercialization of OCM process. Indeed, various works have been reported in the literature involving OCM over monoliths (with well-defined void structure) like metallic monolits [23], ceramic monolits [24], porous SiC [25] and granulated silica based support [26] with limited success.

The monolithic silica (monosil) is a porous single piece of material that can be produced in the dimension of centimeters with various geometries using molds (for example as cylinders). They can be prepared in larger dimensions and used directly in larger reactors, or large number of small size monoliths can be placed into multiple channels; this way risk of changing the void structure of the material during scale up is avoided. Hence, monolithic silica can be a good alternative to the forms of silica used for OCM process by various investigators cited above; however, as far as we know, it has not been used for OCM process although there are some published works involving its preparation and use in other reactions [27–29].

In this work, OCM process over monosilic $Mn/Na_2WO_4/SiO_2$ catalyst was studied; the monosil is prepared using three different methods (1) preparation of monosil followed by Mn and Na_2WO_4 impregnation, (2) Na_2WO_4 impregnation on monosil, in which Mn was inserted during gelation of monosil, and (3) Mn and Na_2WO_4 impregnation over monosil prepared as MCM-41 silica. The reactions test were conducted at various temperatures and feed compositions; the catalysts were also characterized by SEM/EDX and XRD analyses.

2. Experimental

2.1. Catalyst preparation

Particulate Catalyst: 2 wt.%Mn- 5 wt.% Na_2WO_4/SiO_2 was prepared by incipient to wetness sequential impregnation over 60–100 mesh (0.250–0.149 mm) silica gel; Mn was impregnated first. $Mn(NO_3)_2$. $4H_2O$ and Na_2WO_4. $2H_2O$ were used as precursor. After impregnation of each metal, the slurry was dried at 130 °C in the oven, and then calcined at 800 °C for 8 h.

Monosil Catalyst: Monolithic silica (monosil) catalysts were prepared using three different procedures. First, the distilled water, 69% nitric acid, TEOS and PEG 20 000 was added and continuously stirred at 0 °C in a programmable water bath until the solution was turned into a gel. The mixture was then poured into the plastic molds, which had the appropriate diameters for catalysis to be fixed in the reactor after all steps were finished. Then, the molds were kept in the oven at 40 °C for 5 days in order to complete the gelation. Later, monolithic columns were removed from the molds, washed with distilled water and treated with ammonium solution in order to obtain well-ordered mesopores (Fig. 1a). Then they were dried and calcined at 550 °C for 5 h with a ramp rate of 1 °C/min (Fig. 1b). Based on the weight of the monosil, appropriate amount of the $Mn(NO_3)_2$ tetrahydrate solution and then Na_2WO_4 dihydrate solution were poured over the monosil using a disposable plastic transfer pipette. The impregnated monosils were dried (Fig. 1c), and finally calcined at 800 °C for 8 h (Fig. 1d); the catalyst prepared this way was labeled as *monosil* in the remaining part of the manuscript. Although there are some local non-homogeneities in the

colors of monoliths, the procedure was reproducible; the catalyst prepared in different batches gave approximately the same results.

In the second procedure, the manganese was added to the solution before the gelation took place to increase the homogeneous dispersion of the metal precursors. The remaining steps were similar to those in the first method. The monosil prepared this way was labeled as *Mn-monosil*. Finally, as the third method, MCM-41 silica monoliths were prepared by adding CTAB (Cetyltrimethylammonium Bromide) into the solution as a final component to increase the mesoporosity in the monosil followed by calcination and impregnations steps as explained in the first method. This monosil was labeled as *MCM-monosil*.

The last calcination step (800 °C) was initially performed in both muffle furnace (at stationary air) and in the reactor (in flowing air); the catalysts calcined in muffle furnace gave better selectivity and yield; hence the experiments were continued with the samples calcined this way.

2.2. SEM/EDX and XRD characterization

SEM/EDX characterization tests were carried out using Philips XL 30 ESEM-FEG system with the resolution of 2.0 nm (at 20 kV). XRD analysis was performed using Rigaku D/MAX-Ultima+/PC X-Ray diffraction (XRD) equipment having a X-ray generator with Cu Kα radiation (λ = 0.154 nm), scanning angle range of 3–90° at a rate of 2°/min, accelerating voltage of 40 kV and a current of 40 mA in Advanced Technologies Research and Development Center of Boğaziçi University.

2.3. Reaction tests

The catalytic reaction tests were carried out in 10 mm ID, 800 mm long flow quartz reactor, which was narrowed to 2 mm ID after the catalyst bed. In each experiment, 0.3 g particulate catalyst or 2 pieces of monosil (equivalent to 0.3 gr particulate catalyst in weight) were loaded into the reactor; the feed flowrate was 120 ml/min. The upper and lower parts of the reactor were filled with quartz chips to minimize the pre and post-catalytic gas phase reactions. Quartz wool was placed above and below the catalyst bed to prevent the mixing of the catalyst and quartz chips. Temperature was controlled with a K-type thermocouple which was attached to the outer wall of the reactor. The catalyst bed was heated to the reaction temperature under the nitrogen flow. The inlet gas flowrates were measured using mass flow controllers while the total gas flowrate in the reactor outlet was measured by soap bubble meter. The exit stream was analyzed by using a Shimidzu 14A type of GC equipped with TCD detector and Carboxen-1000 60/80 column.

3. Results and discussion

Some researchers suggested that the reactor diameter should be reduced after the catalyst bed and/or the empty space after (and before) the catalyst bed should be filled with quartz chips in order to improve C_2 selectivity [9,17,22,23]. Indeed, we decreased reactor diameter from 10 mm to 2 mm after the catalyst bed, and improved C_2 selectivity significantly even though the conversion was not affected. Similarly, the performance was also improved by filling the empty space before and after the catalyst bed by quartz chips; hence we continued all reactions under these conditions. We did not change the chemical composition of the catalyst considering that 2 wt.%Mn- 5 wt.% Na_2WO_4/SiO_2 was found to be optimum by various investigators.

Following equations were used to calculate CH_4 conversion, C_2 selectivity and yield.

$$CH_4 \, Conversion = \frac{X_{CH_{4in}} \times F_{in} - X_{CH_{4out}} \times F_{out}}{X_{CH_{4in}} \times F_{in}}$$

(1)