



## Review

## Revisiting the oxidative coupling of methane to ethylene in the golden period of shale gas: A review

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## ABSTRACT

Catalytic upgrading of methane in natural gas and/or shale gas via oxidative methane coupling (OMC) is an important option tailored by industry for meeting the global ethylene demand. The paper carefully captured and analyzed recent literature on the progress made regarding the OMC reaction. The review covers issues related to the catalytic strategies adopted for enhancing methane conversion, improving ethylene yield and lowering the reaction temperatures. The potentials and challenges of shale gas as an alternative to natural gas for the OMC process were adequately highlighted.

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## Introduction

The shale gas, which stands as the fossil natural gas accumulated in shale formations, is recently gaining attention as a source of energy and petrochemicals. Clearly, the projected future global escalations in energy demands hinted that, the major roles that conventional natural gas will play are associated with certain uncertainties [1,2]. Therefore, the exploration and utilization of

shale gas could play an important role in addressing some of these uncertainties [3–8]. According to the recent statistics, the shale gas production in the United States had experienced a pronounced increase over the years (i.e. between 2007 and 2013) (Fig. 1), with projections that the trend will continue for the future [9]. Technically recoverable deposits of shale gas are widely distributed across the globe, with major deposits in the countries in Asia, Europe, U.S. and Latin America (Fig. 2) [10–13]. Therefore, there could be a high tendency of improved shale gas production in these parts of the world. In countries like the United States and Canada, shale gas had been gradually replacing the conventional natural gas in many areas of applications, creating significant changes in the market. The main areas of applications currently identified include automobiles and transportations, electricity/power generation,

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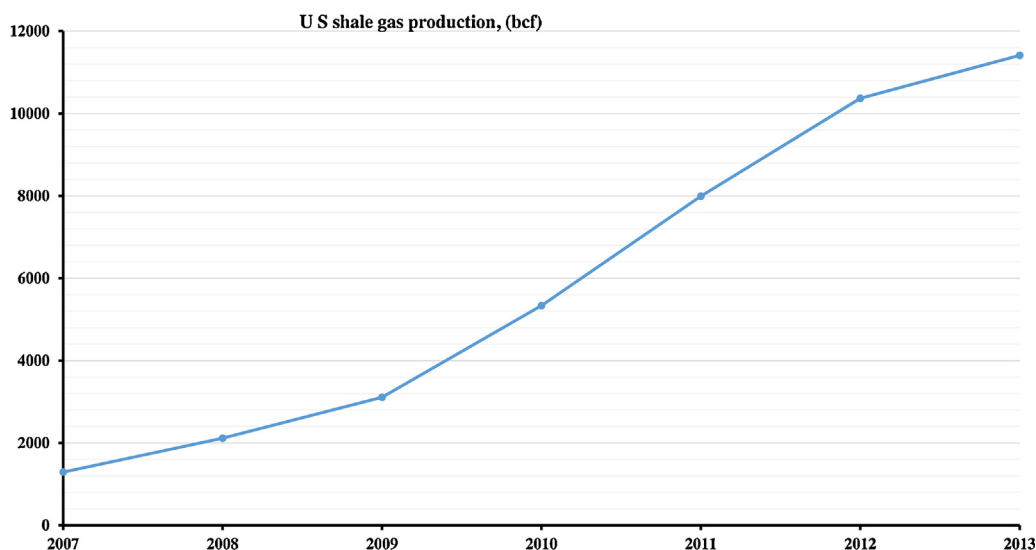


Fig. 1. Shale gas production in billion cubic feet from 2007 to 2013 in the United States (Data source: Ref. [9]).

residential heatings, industrial and commercial applications. Power generation and industrial applications have so far accounted for 30.4% and 29.6% of the market size, respectively [14]. Transportation had been identified as the fastest growing sector, with a projected market rise by 10.8% between 2014 and 2020. According to the overall statistics, the world shale gas market for commercial purposes could grow by 5.3% between 2014 and 2020, amounting to \$9.19 billion [14].

On the basis of the above details, the shale gas production has some considerable potentials for sustaining future global energy demands. Among the prospective areas of industrial applications, conversion to petrochemicals like ethylene will play a great role. Since 1980s, global chemical companies have been making plans to develop an economical process that can upgrade methane gas obtained from conventional natural gas directly into ethylene, an important petrochemical with >137 million metric tons global usage in 2013 alone, indicating that the shale gas would also be employed for its production. The majority of the research for the direct conversion gave emphasis to a process called oxidative coupling, which proceeds by the catalytic reaction of methane with oxygen, through important high temperature steps to produce ethylene [15–20]. However, one noticeable challenge with shale

gas exploration for OMC is its ethane concentration compared to methane. The high ethane level may encourage the refineries to emphasize on cracking rather than the OMC technology. But, investigations of both processes are still critical as the OMC process involved mechanistic stages where ethane is initially produced for further transformation to ethylene. Thus, the ethane concentration may be an added advantage.

The paper will therefore present a concise but critical review on the progress made, regarding the oxidative methane coupling (OMC), and tailor how the future trends in shale gas production may benefit from the technology in addressing global energy and petrochemicals demand. Emphasis would be given to the catalysts evaluated, associated activities and the prospects of nanowires as potential commercialization catalysts. Another vital issue with methane valorization is coke deposition with time [21–24]. Issues related to catalyst composition (i.e. the key active components of the catalyst that promote catalytic activity) and catalyst lifetime will also be simultaneously discussed. An important review on the oxidative methane coupling was the work of Lunsford [15], published in 1995. The work gave emphasis to parameters such as methane activation over the metal oxide surfaces, mechanism of ethylene and ethane formation involving radicals' production and

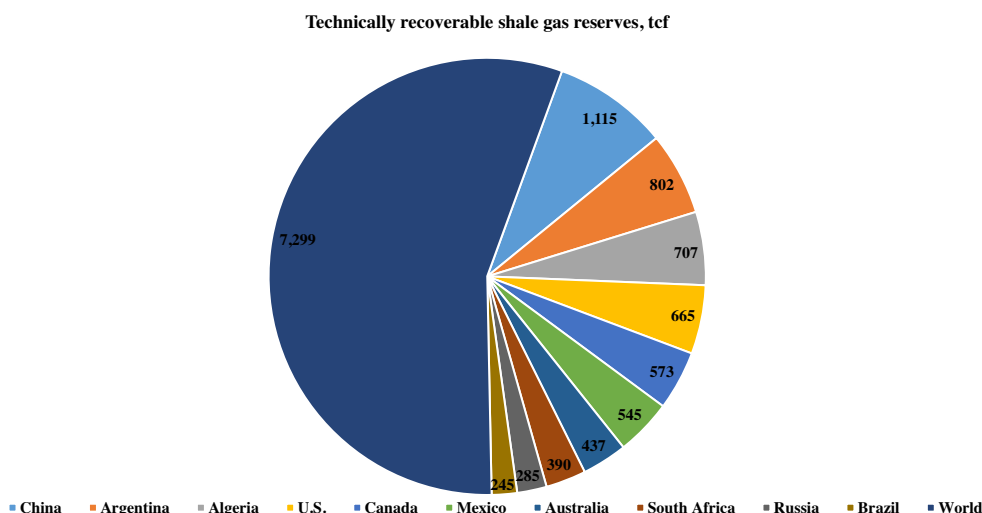


Fig. 2. Technically recoverable shale gas reserves in trillion cubic feet for the main global countries (Data source: Ref. [10]).

coupling and the key reaction centers of the catalysts. It was reported that, the best catalysts within that period were those that produced a methane conversion (i.e. the amount methane transformed) of 20% and combined ethylene and ethane selectivity of 80% [15], indicating that the percentage of unwanted reaction products generated reached 20%. Our current review will therefore tailor recent studies with the view of identifying the progress made. In 2012, Takanabe [25] have also reviewed good number of literature on the main reaction mechanisms. His findings include substantial argument on the formation of gaseous  $\text{H}^\bullet$ ,  $\text{OH}^\bullet$  and  $\bullet\text{CH}_3$  radicals during some intermediate steps of the reaction. Others include the coupling of two  $\bullet\text{CH}_3$  radicals to produce ethane, which can subsequently be oxidized to ethylene in the presence of oxygen. The author further kinetically demonstrated the role of water during the reaction. When water is available in the feed in significant concentrations, activation would be favored than is much possible through hydrogen abstraction from methane. Generated  $\text{OH}^\bullet$  radicals predominantly activate methane than is possible with surface  $\text{O}^\bullet$  sites. These  $\text{OH}^\bullet$  radicals were reportedly believed to be generated from an equilibrated interaction of oxygen with water. Takanabe [25], later reported that, further investigations involving improved catalysts design and optimal selection of reaction conditions with the view of enhancing ethylene yields (i.e. the cumulative amount of ethylene generated during the reaction) and promoting how the oil and gas industry can properly utilize the available findings are still required. These details will therefore be carefully tailored in this review paper.

### Methane to ethylene

The most common technologies adopted by the petroleum refineries for the production of ethylene are the steam and thermal cracking processes. The global ethylene production mainly relied on these processes [26]. In these processes, heat is required to break both the C–C and C–H bonds in heavier fractions, to generate smaller molecules and consequently ethylene [27–31]. A major identified problem here is the energy intensiveness and environmental unsustainability involved [32–35]. It had been established that, up to three tons of  $\text{CO}_2$ , a dangerous greenhouse gas, could be emitted for every single ton of ethylene produced [36,37]. For these reasons, effort to develop simpler, cheaper and sustainable option for the ethylene production had been on track since the last three decades [16]. Owing to the abundant global natural gas deposits and the discovery of huge technically recoverable shale gas deposits, oxidative methane coupling (OMC) had been studied as potential solution. As illustrated in Fig. 2, there is a total of 7299 tcf of technically recoverable shale gas reserves in ten major world countries. Among these countries, China and Argentina dominated with huge reserves of 1115 and 802 tcf, respectively. Similarly, seven out of the ten countries (i.e. 70% of the countries) are having reserves greater than 400 tcf each.

The OMC process involved sequential partial oxidation of methane into ethane and subsequently ethylene (Fig. 3).

Initially, methane reacts with oxygen to produce ethane and water. Through an in situ conversion steps, the ethane generated is subsequently transformed into ethylene, with the possibility of producing higher hydrocarbons in trace quantities. Unfortunately, any slight increase in oxygen concentration can shift the exothermic reaction toward the formation of CO and  $\text{CO}_2$ . The type of oxygen feed (i.e. pure oxygen or air) is another factor be considered by the industries. Carrying out the reaction with pure oxygen will require an air separation unit, consequently increasing the process cost. However, this can potentially be mitigated by employing air directly for the reaction. Another advantage of direct air usage is the possibility of nitrogen in the air to handle the exothermic temperature rise during the reaction. Another important option

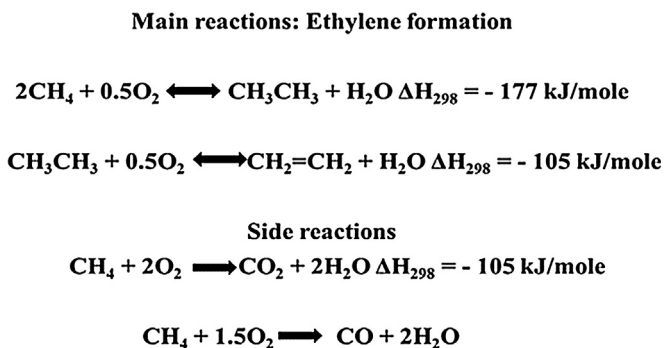


Fig. 3. Catalytic routes for the oxidative methane coupling (OMC) to ethylene reaction.

is the incorporation of dense selective membrane reactor that allows the provision of required oxygen (almost pure) without the need for having an air separating unit. This option can eliminate the challenges such as cost implications and technological difficulties associated with direct air usage. According to Al-zahrani et al. [38], the presence of  $\text{CO}_2$  in the reaction feed can also influence catalytic activity. It lowers the rate of production of ethane and ethylene with negligible effect on their selectivity. As shown in Fig. 4, the  $\text{CO}_2$  can undergo competitive adsorption with  $\text{CH}_4$  and  $\text{O}_2$  at the catalyst surfaces. The interaction of the adsorbed  $\text{CH}_4$  and  $\text{O}_2$  generates radical species and consequently ethane and ethylene. On the other hand, the interaction of adsorbed  $\text{CH}_4$  and  $\text{CO}_2$  changes the reaction pathway to the formation of CO and  $\text{H}_2\text{O}$ .

The main difficulty with OMC is developing an industrially reliable and stable catalyst and the possibility of carrying out the reaction at low temperatures. In view of these numerous studies have been conducted, the recent and most critical of which would be documented in this paper. The first attempt to convert methane into ethylene and other hydrocarbons directly, could be traced to the works of Ito and Lunsford [39], Hinsen and Baerns [40], Keller and Bhasin [41] and Driscoll et al. [42], during the 1980s. These early studies reported that, methane can be successfully converted into ethylene and other hydrocarbons like ethane and benzene to low conversion and sometimes poor yields over metal oxide catalysts. For example, Hinsen and Baerns [40] reported 5% conversion of methane using  $\text{PbO}/\text{Al}_2\text{O}_3$  catalyst with ethylene selectivity of 58% while Ito and Lunsford [39] found 28% methane conversion and 50% selectivity to ethylene. Therefore, the target of most studies following these investigations focused significantly on the effects of catalyst compositions, modifications and reaction conditions toward achieving high conversion and selectivity. The

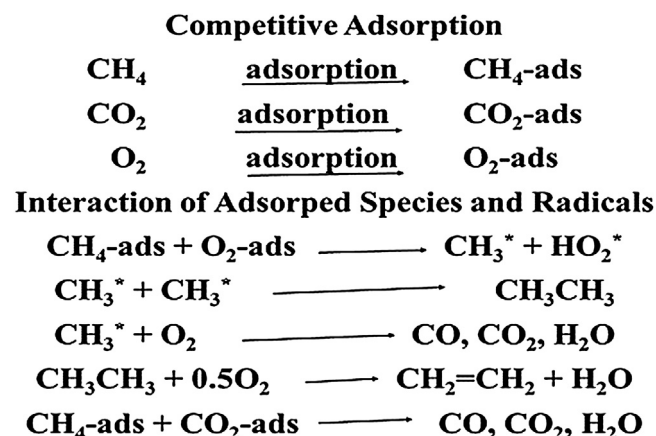


Fig. 4. Influence of  $\text{CO}_2$  on the OMC reaction.

choice of an appropriate catalyst system, reaction conditions and methane to oxygen ratio are very essential to prevent unwanted reactions like the direct conversion of methane to methanol. Some recent studies demonstrated that, methanol can be produced to reasonable yields in a single step from methane over metals supported oxide catalysts [43–48]. Therefore, careful design of the catalyst and selection of reaction conditions are very necessary.

Methane activation can also be achieved through the non-oxidative coupling processes (i.e. high temperature coupling and two step methane homologation). The high temperature coupling process involved the splitting of C–H bond in methane, making the process highly endothermic. Therefore, challenges such as poor catalyst stability and rapid methane decomposition to coke and hydrogen have limited the prospect of the process. On the other hand, the two step homologation method can be achieved at low temperatures in the range of 100–500 °C. Methane initially decomposes followed by surface hydrogenation in the second stage into C<sub>2</sub>+ hydrocarbon compounds. The major challenges with this technology are the poor selectivity to ethylene and low catalyst activity. For these reasons, the OMC reaction still remains more attractive for the industry.

### Catalysts for oxidative methane coupling

The main catalysts employed in the OMC reaction are the oxide catalysts. These can be pure or modified oxides of the transition metals or the mixed or promoted oxides of group IA and IIA elements [49–53]. These systems are developed under different synthesis conditions such as sol–gel, impregnation, precipitation and flame spray pyrolysis to yield variable catalysts compositions with varying basicity properties. Modifications with other oxides, metals or chloride salts coupled with varying reaction conditions such as temperature and space velocity are usually employed to shift the OMC reaction toward improved ethylene selectivity/yield and methane conversion and to limit catalyst deactivation with time [54].

#### Pure or modified transition metal oxides

Pure or unmodified transition metal oxide catalysts are usually associated with low catalytic activity, selectivity to ethylene and rapid lost of catalyst lifetime, and are therefore modified to enhance their catalytic properties. However, some recent studies indicated an improvement with the pure oxides or their mixed counterparts by changing the catalyst preparation conditions like calcination atmosphere. Kuś et al. [55] studied the activities of some pure oxides of transition metals using methane/oxygen ratio 2 and 1400 h<sup>-1</sup> space velocity at 800 °C for 1 h. The effect of catalyst calcination conditions (i.e. in either air or nitrogen) were also evaluated. Irrespective of the oxide nature, calcination with nitrogen reduces methane conversion. For example, with La<sub>2</sub>O<sub>3</sub> the conversions were 40% and 36% when the calcination was conducted in air and nitrogen, respectively. Similarly, the respective values obtained with ZrO<sub>2</sub> were 16% and 12%. Among the oxides, La<sub>2</sub>O<sub>3</sub> catalyst produced the highest ethylene selectivity of 33% that was also constant irrespective of the calcination conditions. Nd<sub>2</sub>O<sub>3</sub> catalyst showed a decreased in selectivity by only 1% (i.e. from 31% to 30%) when calcined in nitrogen, whereas the selectivity reduced from 27% to 23% for the ZrO<sub>2</sub> catalyst. The worst catalytic activity was observed with Nb<sub>2</sub>O<sub>5</sub> catalyst, which produced only 6% methane conversion and 19% ethylene selectivity. This catalyst also produced 80% of CO and CO<sub>2</sub> compared to the highest selectivity of 60% obtained with the most active La<sub>2</sub>O<sub>3</sub> catalyst. The results generally indicated La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> as the most active catalysts due to their higher basicity properties as also demonstrated previously [56,57]. The

basicity-dependent nature of the OMC reaction therefore implies that, any appropriate modification that can enhance the catalyst basicity without destruction to the structural integrity could have positive effect on the overall catalyst performance. Recently, Litawa et al. [58], modified CeO<sub>2</sub> with 33 mol.% each of La<sub>2</sub>O<sub>3</sub> and CaO via the impregnation method and the resulting catalysts were evaluated for OMC reaction at 800 °C and methane oxygen ratio of 3.7 using 0.4 g of catalyst. Without modification, the parent CeO<sub>2</sub>, produced 13.2% methane conversion with 3.3% and 96.7% selectivity to ethylene and CO/CO<sub>2</sub>, respectively. When the catalyst was modified with La<sub>2</sub>O<sub>3</sub>, the conversion and ethylene selectivity increased to 18.4% and 30.2%, respectively whereas the selectivity to CO/CO<sub>2</sub> decreased to 69.3%. On the other hand, the incorporation of CaO onto the parent catalyst further increased the activity to 19.7% conversion and 36.1% ethylene selectivity. Similarly, the CO/CO<sub>2</sub> selectivity dropped to 63%. The presence of CaO promoted the creation of more active basic sites over the parent catalyst than La<sub>2</sub>O<sub>3</sub> and consequently enhanced catalytic activity.

The ability of modified transition metal oxide based catalysts to possess active oxide centers suitable for hydrogen extraction had been considered an important factor for the OMC reaction. According to Ji et al. [59], the presence of WO<sub>4</sub> tetrahedron in the metals promoted W–Mn/SiO<sub>2</sub> provides an opportunity in terms of energy matching with methane and the appropriate geometry for hydrogen extraction, leading to good OMC activity. The authors employed 5 wt.%XWO<sub>4</sub>/Mn/SiO<sub>2</sub> catalysts (where X = Co, Ni or Fe) synthesized via impregnation method for OMC reaction at 800 °C and 0.1 MPa using 0.2 g of catalyst for a period of 5 h. The results of the reaction were dependent on the nature of the metal incorporated into the WO<sub>4</sub> tetrahedron. During the first 30 min, methane conversions were very similar (i.e. 18.3–18.4%). However, after 5 h, the conversions decreased to 17.7%, 18.1% and 17.9% for FeWO<sub>4</sub>/Mn/SiO<sub>2</sub>, CoWO<sub>4</sub>/Mn/SiO<sub>2</sub> and NiWO<sub>4</sub>/Mn/SiO<sub>2</sub> catalysts, respectively (see Fig. 5), indicating a relatively higher stability with the Co containing catalyst. On the other hand, the respective selectivities to ethylene were 7.5%, 11.1% and 10.6%, retaining the best results with the Co catalyst. Ni containing catalyst produced the largest quantity of CO<sub>2</sub> (i.e. 24%). It could be seen that, under these conditions, both conversion and selectivity were low. However, when the transition metals were replaced with Na and K to form 5 wt.%Na<sub>2</sub>WO<sub>4</sub>/Mn/SiO<sub>2</sub> and 5 wt.%K<sub>2</sub>WO<sub>4</sub>/Mn/SiO<sub>2</sub>, methane conversion increased to 30% and was nearly constant for 5 h. Similarly, the selectivity to ethylene increased to 44% and 40% for the Na and K promoted catalysts, respectively. According to previous works [60–62], incorporation of Na or K species promotes surface basicity of the parent catalyst and consequently active interaction with methane. However, appropriate reaction conditions must be selected to ensure enhanced catalytic performance. The work of Lee et al. [63] studied the effect of changing reaction

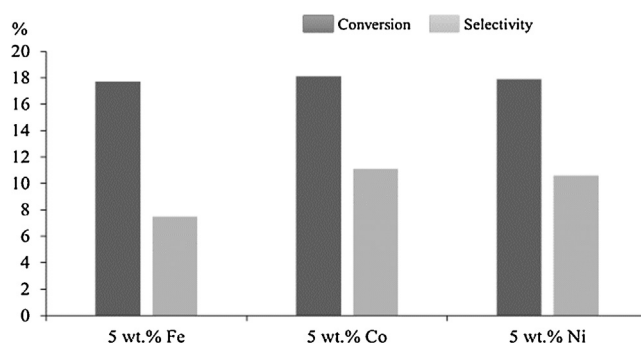


Fig. 5. Effect of metal incorporation on the activity and C<sub>2</sub>-selectivity of WO<sub>4</sub>/2 wt.%Mn/SiO<sub>2</sub>. Reaction conditions; 800 °C and 0.1 MPa, 0.2 g, 5 h (Data source: Ref. [59]).



parameters on the activity of the  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst prepared via impregnation method. It was observed that, at  $10,000 \text{ h}^{-1}$  and methane/oxygen ratio of 5, increasing the reaction temperature from 760 to  $840^\circ\text{C}$  raised the methane conversion from 11% to 20%. Below  $760^\circ\text{C}$ , no reaction was achieved whereas the catalyst deactivates when the temperature exceeds  $850^\circ\text{C}$ . A similar trend was found with ethylene selectivity. However, irrespective of the temperature or methane/oxygen ratio, the ethylene selectivity was below 30%. On the other hand, space velocity was found to have an effect opposite to that of temperature. The lowest value of  $5000 \text{ h}^{-1}$  produced the highest conversion of 25% corresponding to 24% ethylene selectivity at  $840^\circ\text{C}$ . Therefore, a suitable combination of space velocity and temperature is necessary to achieve optimal catalytic performance with the  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst.

Mahmoodi et al. [64] investigated the effect of replacing  $\text{WO}_4$  with  $\text{VO}_3$  or  $\text{CrO}_4$  species in the  $\text{Na}-\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst for the OMC reaction at conditions of  $775^\circ\text{C}$ , 0.1 MPa, 1.8 g of catalyst and a total gas flowrate of  $100 \text{ cm}^3/\text{min}$ . The parent catalyst (i.e.  $\text{Mn}/\text{SiO}_2$ ) was synthesized to contain 2.8 wt.% Mn supported over  $\text{SiO}_2$ . Transition metal oxides were loaded at 4.5 wt.% to obtain the corresponding various modified catalysts. The catalytic activity was reasonably dependent on the modification. Catalyst containing  $\text{WO}_4$  to form  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  produced the highest methane conversion of 42.3% whereas the catalyst containing Cr (i.e.  $\text{Na}_2\text{CrO}_4/\text{Mn}/\text{SiO}_2$ ) produced the lowest conversion of 37%. When the reaction was carried out with  $\text{NaVO}_3/\text{Mn}/\text{SiO}_2$ , the respective methane conversions obtained were 40.6%. The selectivity to  $\text{C}_2$  species was also dependent on the catalyst nature. Catalysts containing  $\text{Na}_2\text{WO}_4$  and  $\text{NaVO}_3$  yielded the highest and lowest selectivity of 36.5% and 9.3%, respectively. On the other hand, catalyst containing  $\text{Na}_2\text{CrO}_4$  produced a corresponding selectivity of 14.6%. It could be observed that, under the employed reaction conditions,  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  formed the best catalyst system both in terms of methane conversion and  $\text{C}_2$ -selectivity. The authors [64] argued that, appropriate interaction of Na and metal oxide is necessary to achieve high selectivity, and therefore attributed the best activity of  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  to most favorable interaction under the conditions studied.

Hiyoshi and Ikeda [65] demonstrated the role of modifying the  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst with molten XCl (X = Na, K, Li or Cs) on the catalytic activity. The molten salts were incorporated into the parent catalyst by ordinary mechanical mixing. Catalysts were evaluated at  $750^\circ\text{C}$  and methane to oxygen ratio of 5.7:3.5 at 0.101 MPa pressure using 0.1 g of catalyst. The catalyst modified with molten NaCl produced the best activity of 55% methane conversion and 31.2% and 56.5% ethylene yield and selectivity, respectively. When both NaCl and KCl were incorporated into the parent  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst, the conversion dropped to 45%, yield to 27.2% whereas the ethylene selectivity increased to 60.4%. On the other hand, LiCl produced the lowest activity of 14.1% methane conversion and 6.4% and 45.3% ethylene yield and selectivity, respectively. However, reverse effect was observed when the reaction temperature was lowered to  $650^\circ\text{C}$ . Catalyst modified with LiCl produced the highest yield of 13% compared to <8% obtained with all other catalysts. It was observed that, the degree of catalyst deactivation with time was also dependent on the nature of the molten salt. Highest stability was observed with NaCl followed by KCl and CsCl yielded the lowest stability properties. The three respective catalysts deactivated after 13, 6 and 1.5 h at  $750^\circ\text{C}$ , consistent with their degree of melting and existence of salt vapor documented in the literature [65–68].

Another alternative way of achieving improved activity with the  $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$  catalyst is varying its  $\text{Na}_2\text{WO}_4$  or Mn content or changing the synthesis method. Recently, Koirala et al. [69] synthesized catalysts of variable Mn and  $\text{Na}_2\text{WO}_4$  compositions by

flame spray pyrolysis and compared the activities with those prepared by the impregnation method. The effect of  $\text{Na}_2\text{WO}_4$  content was evaluated by keeping the Mn content fixed at 1.9 wt.% (i.e. 1.9 wt.%  $\text{Mn}/\text{SiO}_2$ ), and catalytic studies performed at  $800^\circ\text{C}$  using 0.208 g of catalyst. Without  $\text{Na}_2\text{WO}_4$ , the 1.9 wt.%  $\text{Mn}/\text{SiO}_2$  produced low methane conversion of 15% and 2.2% yield of  $\text{C}_2$  species (i.e. ethylene and ethane). Incorporation of 1 and 3 wt.%  $\text{Na}_2\text{WO}_4$  shifted the yield to 13.5% and 16%, respectively, with no any further increase in yield beyond the 3 wt.% loading. At higher loadings, formation of agglomerates and the complete coverage of the active manganese oxide surfaces could significantly lead to the poor catalyst performance [70,71]. The authors [69] also argued that, the existence of distorted  $\text{WO}_4$  tetrahedrons following the modification with Na were very critical for the creation of active centers, as also previously observed elsewhere [59,72,73]. Reactions conducted with the 3 wt.%  $\text{Na}_2\text{WO}_4/\text{SiO}_2$  showed very insignificant activity of <1% methane conversion and <5% yield of the  $\text{C}_2$  species. However, with 3 wt.%  $\text{Na}_2\text{WO}_4/1.9 \text{ wt.}\% \text{ Mn}/\text{SiO}_2$ , the yield increased to 18.5%. The authors [69] further demonstrated that, comparable optimal activities were obtained irrespective of whether the catalysts were prepared by impregnation or flame spray pyrolysis method. It has been established from the study that, to achieve the optimal catalytic performance with these types of catalysts the constituent elements such as Mn, Na, W and Si must be incorporated into the catalyst system in an appropriate ratio. Godini et al. [74] evaluated the activities of a 5 wt.%  $\text{Na}_2\text{WO}_4/1.9 \text{ wt.}\% \text{ Mn}/\text{SiO}_2$  catalyst prepared by sol–gel method and a similar catalyst synthesized using the regular impregnation method. In this case, the catalytic activity was dependent on the method of catalyst preparation (see Fig. 6). When the reaction was carried out at  $825^\circ\text{C}$  and 2.5 methane/oxygen ratio in a fixed-bed reactor, catalyst prepared by impregnation method produced methane conversion,  $\text{C}_2$ -selectivity and yield of 26.5%, 72.2% and 19.1%, respectively. On the other hand, the catalyst prepared by the sol–gel method produced the respective values of 35.4%, 58.1% and 21%, respectively. Therefore, the sol–gel method formed the best catalyst system due to higher  $\text{C}_2$ -yield.

Ivanov et al. [75] studied the role of catalyst composition and microstructure on the activity of  $\text{SrTiO}_3$  and  $\text{Sr}_2\text{TiO}_4$  modified with metals. The catalysts were prepared by mechano-chemical process, involving air sintering at  $1100^\circ\text{C}$  for a period of 4 h. Methane conversions were then conducted at temperatures of  $850$  and  $900^\circ\text{C}$ . Incorporation of metals such as Mg, Ca and Ba produced double-phase catalysts (i.e. substituted  $\text{SrTiO}_3$  and layered  $\text{Sr}_2\text{TiO}_4$  phases). However, when the modification was carried out with Al and Pb, the resulting catalysts were  $\text{Sr}_3\text{Al}_2\text{O}_6$  and  $\text{SrPbO}_3$ , respectively. Catalyst modified with Mg and Al produced the best performance of 66% and 25% selectivity and

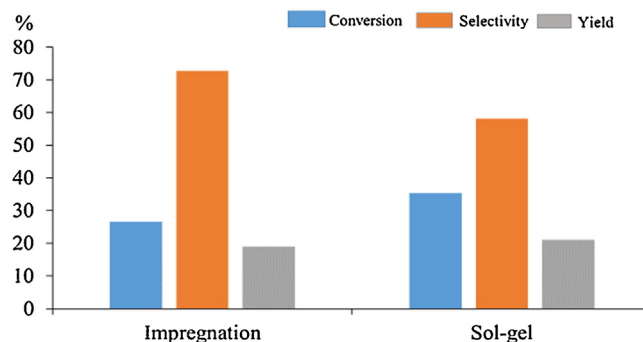


Fig. 6. Effect of preparation method on the conversion,  $\text{C}_2$ -selectivity and yield of 5 wt.%  $\text{Na}_2\text{WO}_4/1.9 \text{ wt.}\% \text{ Mn}/\text{SiO}_2$  catalyst prepared by sol–gel and impregnation methods. Reaction conditions;  $825^\circ\text{C}$  and 2.5 methane/oxygen ratio (Data source: Ref. [74]).

yield of  $C_2$  species, respectively. The superior activity was attributed to the existence of microstructure, which decomposes under reaction conditions producing binary carbonates (i.e.  $SrCO_3$  and  $MgCO_3$  in case of Mg) that were very active for methane activation. Previously, some authors [76] demonstrated the incorporation of Li, Na or Mg into  $BaSrTiO_3$  to produce corresponding  $YBaSrTiO_3$  in which Y stands for the metal modifier, to increase the overall catalytic performance of the parent titanate catalyst ( $BaSrTiO_3$ ). The respective metals were incorporated through impregnation of the corresponding chloride salt solutions. Methane conversions were conducted using 1.5 g of catalyst in the temperature range of 580–850 °C, 40:20 (methane:oxygen ratio) and 6000  $h^{-1}$  space velocity. Without any modification, the parent catalyst produced 47% methane conversion and 29.5% selectivity to  $C_2$  species. Modification with Li reduced the conversion to 37% but increased the selectivity to 59.5%. Catalysts containing Mg and Na produced comparably similar conversion (~47%) with the parent catalyst, but increased the selectivity to 43% and 51%, respectively. Generally, the modified catalysts produced  $C_2$  yields of 20–24% higher than 14% obtained with the parent catalyst under constant reaction conditions.

In Table 1, an informative detail on the behaviors of transition metals-based oxide catalysts reported recently has been presented. The results generally indicated that, catalysts containing  $Na_2WO_4$  are increasingly gaining attention for the OMC reaction in the recent years. They are usually promoted with Mn or supported over different oxide supports to optimize compositional and activity/selectivity properties. According to Lee et al. [77], the nature of oxide modifier significantly influenced the activity of  $Na_2WO_4/Mn/SiO_2$  catalyst, when the OMC reactions were performed at 850 °C and reduced methane/oxygen ratio of 3.5–2.0 in

the presence of 60 mol% nitrogen. Without any modification, the parent powdered  $Na_2WO_4/Mn/SiO_2$  catalyst produced 32% methane conversion and 45% selectivity to ethylene. It could be observed that, incorporation of 3 wt.%  $Al_2O_3$  and 16.7 wt.%  $MgO$  raised the methane conversion to 41% and 50%, respectively, whereas the selectivity changes to 47% and 38%, respectively. On the other hand, modification with 20 and 40 wt.%  $TiO_2$  increased the initial conversion to 41% and 39%, with a similar trend for selectivity to 60% and 59%, respectively. According to these results, oxide modification can have positive effect on both methane conversion and ethylene selectivity. Under the reaction conditions employed, catalyst modified with 20 wt.%  $TiO_2$  produced the best activity (24.6% yield of ethylene) [77]. Ghose et al. [78] developed similar catalyst system (10%  $Na_2WO_4/5\%Mn/SiO_2$ ) via solution combustion method and investigated the effect of Ce or La modification on the ethylene yield at 800 °C, methane/oxygen ratio of 4% and 10% nitrogen. Without any modification, the catalyst yield 18% of ethylene but the yield increased to 20% and 24% when Ce and La were incorporated, respectively. Among the modifiers, La produced the best results attributed to enhancement in active  $WO_4$  tetrahedron structure, suitable for methane activation with W containing catalysts. Oshima et al. [79], reported a very low methane conversion with of 3.8% and 18.4% ethylene selectivity pure  $ZrO_2$  catalyst at 150 °C in the presence of  $CO_2$  under electric field assisted conditions (i.e. 3.0 mA and 800 V). This activity further decreased to 3.0% conversion and 31.2% selectivity when  $ZrO_2$  was modified with 5 wt.% La and the voltage raised to 1200 V. However, a slight increase in activity (i.e. to 6.3% conversion) and 32.3% selectivity was observed when 5 wt.%  $Ba/La_2O_3$  was employed as the catalyst. Generally, all the three catalysts produced activities lower than those obtained with the

**Table 1**  
Recent studies on the behaviors of transition metals-based oxides during OMC reaction.

Catalyst	Reaction condition	Methane conversion, %	Ethylene/ $C_2$ selectivity (S) OR yield (Y), %	$CO_x$ ( $x=1, 2$ ) selectivity/yield, %	Ref.
$Na_2WO_4/Mn/SiO_2$ (powder)	850 °C, 10,000 $h^{-1}$ , $CH_4/O_2=3.5$ , 60 mol% $N_2$	32	45 (S)	Not reported	[77]
$Na_2WO_4/Mn/SiO_2$ modified with 3 wt.% $Al_2O_3$ (pellet)	850 °C, 10,000 $h^{-1}$ , $CH_4/O_2=2$ , 60 mol% $N_2$	41	47 (S)	Not reported	[77]
$Na_2WO_4/Mn/SiO_2$ modified with 16.7 wt.% $MgO$ (pellet)	850 °C, 10,000 $h^{-1}$ , $CH_4/O_2=2$ , 60 mol% $N_2$	50	38 (S)	Not reported	[77]
$Na_2WO_4/Mn/SiO_2$ modified with 20 wt.% $TiO_2$ (extruded)	850 °C, 10,000 $h^{-1}$ , $CH_4/O_2=2$ , 60 mol% $N_2$	41	60 (S)	Not reported	[77]
$Na_2WO_4/Mn/SiO_2$ modified with 40 wt.% $TiO_2$ (extruded)	850 °C, 10,000 $h^{-1}$ , $CH_4/O_2=2$ , 60 mol% $N_2$	39	59 (S)	Not reported	[77]
10% $Na_2WO_4$ –5%Mn/ $SiO_2$ , prepared by solution combustion method	1 g of catalyst, 10% $N_2$ , methane: oxygen = 32:8, 800 °C	Not reported	18 (Y)	Not reported	[78]
10% $Na_2WO_4$ –5% Mn/ $SiO_2$ , prepared by solution combustion method, modified with 5% La	1 g of catalyst, 10% $N_2$ , methane: oxygen = 32:8, 800 °C	Not reported	24 (Y)	Not reported	[78]
10% $Na_2WO_4$ –5% Mn/ $SiO_2$ , prepared by solution combustion method, modified with 5% Ce	1 g of catalyst, 10% $N_2$ , methane: oxygen = 32:8, 800 °C	Not reported	20 (Y)	Not reported	[78]
Pure $ZrO_2$	200 mg of catalyst, 18 $h^{-1}$ , 150 °C (in electric field, 3.0 mA, 800 V)	3.8	18.4 (S)	81.6	[79]
5 wt.% La/ $ZrO_2$	200 mg of catalyst, 18 $h^{-1}$ , 150 °C (in electric field, 3.0 mA, 1200 V)	3.0	31.2 (S)	68.8	[79]
5 wt.% Ba/ $La_2O_3$	200 mg of catalyst, 18 $h^{-1}$ , 150 °C (in electric field, 3.0 mA, 600 V)	6.3	32.3 (S)	67.7	[79]
$Mn_xO_y$ – $Na_2WO_4$ supported over SBA-15	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 1, 16 h	14	70 (S)	Not reported	[80]
$Mn_xO_y$ – $Na_2WO_4$ supported over commercial $SiO_2$ (D11-10)	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 1, 16 h	7	58 (S)	Not reported	[80]
$Mn_xO_y$ – $Na_2WO_4$ supported over $SiO_2$ -gel (grade 923)	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 1, 16 h	2	50 (S)	Not reported	[80]
5 wt.% $Na_2WO_4/La_2O_3$	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 4, 16 h	10	30 (S)	Not reported	[81]
5 wt.% $Na_2WO_4/SiO_2$	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 4, 16 h	5	40 (S)	Not reported	[81]
5 wt.% $Na_2WO_4/Fe_2O_3$	750 °C, 50 mg catalyst, methane/oxygen = 4, $N_2$ ratio = 4, 16 h	3	60 (S)	Not reported	[81]

$\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ -based catalysts by Lee et al. [77] and Ghose et al. [78], making them less attractive under the reaction conditions used. Another unfavorable factor observed was the production of CO and  $\text{CO}_2$  species to very high selectivity (67–82%). According to a study by Yildiz et al. [80], the nature of the  $\text{SiO}_2$  support employed could significantly affect the catalytic performance of  $\text{Mn}_x\text{O}_y$ - $\text{Na}_2\text{WO}_4/\text{Mn}$  catalyst at temperature of 750 °C and methane to oxygen ratio of 4 in 16 h. Incorporation of SBA-15 produced the best results (14% methane conversion and 70% selectivity) whereas the worst results were obtained when  $\text{SiO}_2$ -gel (commercial grade 923) was employed as the support. The resulting catalyst produced 2% methane conversion, the worst of all the conversions reported in Table 1, with 50% selectivity to ethylene. Reaction with  $\text{SiO}_2$  (commercial D11-10) as support also yield a reduction in these values to 7% conversion and 58% selectivity. However, the resulting catalyst was more active compared to the commercial  $\text{SiO}_2$ -gel supported catalyst. In another study the same authors [81], demonstrated that replacing  $\text{SiO}_2$  by  $\text{Fe}_2\text{O}_3$  or  $\text{La}_2\text{O}_3$  can influence the catalytic activity of a 5 wt.%  $\text{Na}_2\text{WO}_4$  catalyst under comparable reaction conditions (i.e. 750 °C and 16 h). When the reaction was carried out with  $\text{SiO}_2$  as support, the conversion and selectivity were 5% and 40%, respectively. The decreased in activity with the overall catalyst (5 wt.%  $\text{Na}_2\text{WO}_4/\text{SiO}_2$ ) compared to that obtained in the former study [80], could be due to the absent of Mn modifier in the catalyst. Incorporation of  $\text{La}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  produced respective methane conversions of 10% and 3% and corresponding selectivities of 30% and 60%, further indicating that, the addition of Mn to  $\text{Na}_2\text{WO}_4$  is necessary to achieve enhanced catalyst performance [80,81].

#### Group IA and IIA catalysts

Early OMC reactions conducted in the 1990s with catalysts based on group IA and IIA compounds gave emphasis mainly to the activity of pure or mixed oxide systems, with much interest on MgO or its mixture with other oxides like BaO, CaO and  $\text{Li}_2\text{O}$  [51,82–87]. Those studies concentrated principally on issues related to resolving the complex mechanism associated with the reaction [88,89]. However, this was demonstrated to proceed by a combination of homogeneous and heterogeneous processes [90–92]. It was established that, the critical role of the catalyst is to provide desirable surface sites for homolytic methane activation to generate radical species, with the possibility of subsequent reaction to produce hydrocarbons [15,93–95]. Limited effort was devoted on the main role of catalyst structure/morphology, however the high reaction temperatures required to activate methane with these materials could be reduced and on the possibility of attaining commercially viable methane conversion and ethylene selectivity/yield. These challenges remained the subjects of research in the recent times [96–99]. Recently, Gao et al. [100] conducted a study with catalysts based on  $\text{BaCO}_3$  and MgO under variable temperature conditions. For reactions carried out with  $\text{BaCO}_3$  using methane/oxygen ratio of 4, methane conversion increased with increase in temperature. At 780 °C the conversion was 10.3% but increased to 24.7% when the temperature was raised to 860 °C. On the other hand, selectivity to  $\text{C}_2$  species decreased, whereas the production of  $\text{CO}_x$  ( $x = 1$  and 2) increased. At 780 °C, the  $\text{C}_2$  selectivity was 48.5%, whereas the selectivity for  $\text{CO}_x$  was 51.6%. When the temperature was raised to 860 °C, the respective selectivities were 35% and 65%. Reactions conducted with MgO as catalyst produced trend that shows some deviation. Initially, the methane conversion increased from 23.6% at 740 °C to 24.9% at 820 °C but decreased to 24.2% when the temperature was further raised to 860 °C (see Fig. 7). Selectivity to  $\text{C}_2$  increased from 34.5% at 740 °C to 41.8% at 820 °C before decreasing to 29.4% when the

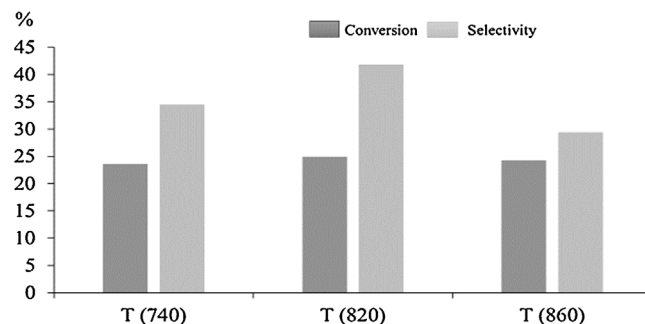


Fig. 7. Effect of reaction temperature ( $T$  °C) on the activity and  $\text{C}_2$ -selectivity of MgO catalyst using  $\text{CH}_4/\text{O}_2 = 4$  (Data source: Ref. [100]).

temperature was raised to 860 °C. The results indicated MgO as the most active catalyst than  $\text{BaCO}_3$  under constant reaction conditions. It could be seen that, the MgO catalyst produced optimal values (i.e. 24.9% conversion and 41.8%  $\text{C}_2$  selectivity) at 820 °C. The conversions at low temperatures were also higher for this catalyst.

Catalysts based on MgO have demonstrated good activity and stability properties in the OMC reaction when modified with alkali metals like Li and Na or co-modified with transition metals. According to Gao et al. [100], incorporation of 3 wt.% Li over the MgO catalyst promoted the catalytic performance at 780 °C. The methane conversion increased to 30% from an initial value of 23% when the reaction was carried out without modification. The  $\text{C}_2$  selectivity also increased to 62% from an initial value of 43%. Therefore, the addition of Li as modifier had a positive effect of increasing the rate at which the coupling of methyl radicals on the catalyst surface takes place. Simon et al. [101] investigated the effect of co-doping Li with some transition metals (i.e. Fe and Gd) over the MgO. Catalytic studies were conducted at 750 °C using 50 mg of catalyst and methane/oxygen/nitrogen ratio of 4:1:4. Reaction with unmodified MgO produced a very low methane conversion of 2% and  $\text{C}_2$  selectivity of 32% that were apparently stable for 16 h. When Li was incorporated, the conversion initially reached 10% but dropped to 4% in 2 h and remained stable for 16 h. On the other hand, the  $\text{C}_2$  selectivity remained constant at 52% for the 16 h period. The effect of Li addition is therefore in good agreement with the previous work [100]. When both Fe and Gd were co-doped over MgO, the conversion increased to 16% and was stable for 16 h. The  $\text{C}_2$  selectivity decreased to 22% and later to 20% after 4 h. Co-doping of Gd and Li produced 15% methane conversion that reduced to 12% after 2 h whereas the selectivity remained constant at 45% for the 16 h period. According to these results, co-presence of Li and Fe or Gd have positive effect on methane conversion with a negative effect on  $\text{C}_2$  selectivity, but overall the modification produced positively higher yields of  $\text{C}_2$ , especially with the Gd–Li/MgO catalyst. These results showed good agreement with the trend reported by Arndt et al. [102]. Similarly, the modification appeared to promote catalyst stability with time.

Rane et al. [103] studied the role of alkali metal content on the activity of CaO catalysts. Alkali metals were loaded to CaO in the ratio of 0.1–0.4 for a metal/CaO. Reactions were conducted at 700–750 °C, methane/oxygen ratio of 4 and a space velocity of  $5140 \text{ h}^{-1}$ . At a particular metal/CaO ratio, the conversion of methane increased with increase in temperature. For example, the conversions at 700 °C for Li/CaO, Na/CaO and Cs/CaO when the metal/CaO ratio was 0.1 were 4.6%, 11.5% and 8.0%, respectively. These respective values increased to 12.8%, 24.7% and 22.8% when the temperature was raised to 750 °C (see Fig. 8). A similar trend was observed with the  $\text{C}_2$  selectivity. At this metal/CaO ratio of 0.1, the selectivities were 65.3%, 56.0% and 34.8% at 700 °C for the respective catalysts but increased to 68.0, 61.6 and 49.1% when the



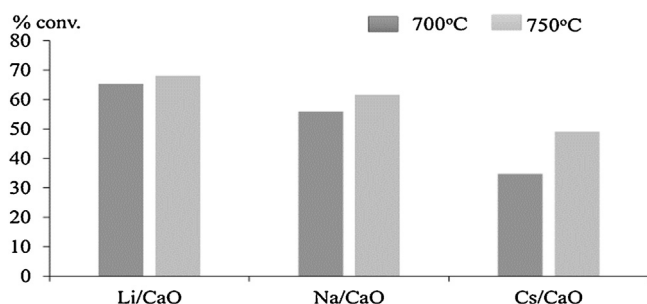


Fig. 8. Effect of temperature on CH<sub>4</sub> conversion for Li/CaO, Na/CaO and Cs/CaO catalyst when the Metal/CaO ratio was 0.1 (Data source: Ref. [103]).

temperature was raised to 750 °C (see Fig. 9). However, the situation was different when the metal/CaO ratio was changed from 0.1 to 0.4. For Li/CaO catalyst, increasing the ratio from 0.1 to 0.4 increased the methane conversion from 12.8% to 22% at 750 °C whereas the selectivity decreased from 68% to 62% at 750 °C. With Na/CaO, the conversion decreased from 24.7% to 17.9%, whereas the selectivity slightly increased from 61.6% to 62.6% under these conditions. When Cs/CaO was employed as the catalyst, conversion also decreased from 22.8% when the metal/CaO was 0.1–11.0% when the ratio was raised 0.4. However, the selectivity increased from 49.1% to 69.9%. The overall results showed that, at the metal/CaO of 0.1, the methane conversion follows the order Li/CaO > Na/CaO > Cs/CaO. This trend is consistent with the corresponding basicity of the catalysts. However, no peculiar trend could be established when the ratio reached 0.4. The authors [103] proposed the reaction to involve the production of methyl peroxide radicals (i.e. CH<sub>3</sub>OO•) at the intermediate stages of the reaction. Therefore, the increased in the selectivity of C<sub>2</sub> species with temperature could be attributed to the decomposition of these radicals due to their low stability at high temperatures, with a net decreased in the production of CO<sub>2</sub>.

There are indications that, transition metals could be employed instead of the alkali metals as catalyst modified for the CaO catalyst. Rane et al. [104] showed La as a good promoter for CaO catalyst when the La/Ca is 0.05, with the effect being dependent on the La or CaO source. The authors conducted the reactions at 800 °C by employing methane to oxygen ratio of 4 and 51,360 h<sup>-1</sup> space velocity. Modification with La from La(NO<sub>3</sub>)<sub>3</sub> produced 22.5% methane conversion and 53.4% C<sub>2</sub>-selectivity whereas the incorporation of (CH<sub>3</sub>COO)<sub>3</sub>La as La source yields 25.7% conversion and 49.8% selectivity. In both cases CaCO<sub>3</sub> was employed as the main CaO source. However, when the CaO source was changed to (CH<sub>3</sub>COO)<sub>2</sub>Ca, the conversion and selectivity changed to 28.1% and 52.5%, respectively. Therefore, the oxide precursor and the method of catalyst preparation should be critically considered when designing an effective OMC catalyst.

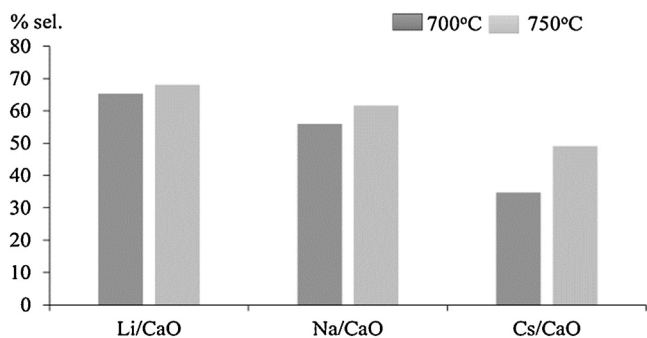


Fig. 9. Effect of temperature on C<sub>2</sub>-selectivity for Li/CaO, Na/CaO and Cs/CaO catalyst when the Metal/CaO ratio was 0.1 (Data source: Ref. [103]).

Machocki and Jezior [105] performed a study with Na/CaO catalyst modified with Cl<sup>-</sup> ions of which the Na content was 3.0 wt.% whereas the loading of Cl<sup>-</sup> was varied from 0 to 11.08 wt.%. Both methane conversion and products yield were dependent on the chloride content. When a reaction was conducted at 800 °C using methane/oxygen ratio of 20:1, the methane conversion was 9% with Na/CaO but decreased to 3% when 11 wt.% of chloride ions was doped. When the methane to oxygen ratio was reduced to 10:1, the conversion initially increased to 14% for Na/CaO but dropped to 5% for the chloride loadings between 2 and 11 wt.%. On the other hand, the yield of C<sub>2</sub> species decreased from 8% to 3% when the ratio was 20:1 and from 12% to 5% when the ratio was reduced to 10:1. The modified catalysts produced mainly C<sub>3</sub><sup>+</sup> hydrocarbons than the desired ethylene. The ethylene selectivity was basically in the range of 30–40% irrespective of the chloride content. Addition of chloride ions reduces catalyst basicity by neutralizing the strong basic sites at the catalyst surface [106–109]. This poisoning effect decreases the number of active sites and consequently favor complete oxidation of hydrocarbons into CO<sub>x</sub> species. However, according to Wang et al. [110], the incorporation of BaCl<sub>2</sub> to TiO<sub>2</sub> and SnO<sub>2</sub> can increase both methane conversion and ethylene selectivity. For reactions conducted at 800 °C using methane/oxygen ratio of 2 and 5000 h<sup>-1</sup> space velocity, BaCl<sub>2</sub> produced 6.5% conversion. However, when loaded over TiO<sub>2</sub> and SnO<sub>2</sub> the conversion increased to 32.0 and 38.3%, respectively. Similarly, the conversion was further raised to 43.8% when BaCl<sub>2</sub> was loaded to TiO<sub>2</sub>–SnO<sub>2</sub> composite. On the other hand, the ethylene selectivity with BaCl<sub>2</sub> was 14.4% but increased to 47.5 and 39.4% when loaded over TiO<sub>2</sub> and SnO<sub>2</sub>. The corresponding selectivity with the BaCl<sub>2</sub>/TiO<sub>2</sub>–SnO<sub>2</sub> catalyst was also raised to 45.8%. The presence of BaCl<sub>2</sub> in TiO<sub>2</sub> and SnO<sub>2</sub> enhances the formation of activated oxygen species that can interact with methane to produce methyl radicals as also observed previously [111,112].

Baidya et al. [113] conducted the reaction with mixed oxides based on SrO and Al<sub>2</sub>O<sub>3</sub> synthesized from co-precipitation of the corresponding metal hydroxides. The Sr/Al in the catalysts was varied from 0 to 1.5. Reactions were performed using 300 mg of catalyst at 810 °C and total methane and oxygen flow of 130 mL/min. The results of the study showed the Sr/Al to influence both conversion and selectivity. Increasing this ratio from 0 to 1.25 increased linearly the methane conversion from 14% to 28%. However, further raising the ratio to 1.5 reduced the conversion drastically to only 6%. On the other hand, selectivity of C<sub>2</sub> species increased from 16 when the ratio was 0–64% when the ratio was raised to 1.5. For comparison, other reactions were conducted with SrCO<sub>3</sub>, Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and the widely studied Na<sub>2</sub>WO<sub>4</sub>/Mn/SiO<sub>2</sub> catalyst. With SrCO<sub>3</sub>, the methane conversion was similar to that obtained with the least active catalyst having the Sr/Al ratio of 1.5 (i.e. 6%). Unfortunately, the selectivity was lower by 3%. On the other hand, Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> produced methane conversion that was comparable to that of the most active catalyst having Sr/Al ratio of 1.25 but the selectivity decreased by 9%. The Na<sub>2</sub>WO<sub>4</sub>/Mn/SiO<sub>2</sub> catalyst produced the highest selectivity of 68% compared to all other catalysts but its conversion was 18% (i.e. 10% lower than that obtained with the most active catalyst containing Sr/Al of 1.25). Previously, Gayko et al. [114] found the doping of 1.0 wt.% SrO over Nd<sub>2</sub>O<sub>3</sub> as an effective way of promoting the OMC reaction activity. Without SrO, the parent catalyst yields 10.9% methane conversion at 800 °C. However, this value increased to 12.5% when 1.0 wt.% SrO was added. The C<sub>2</sub> selectivity also increased from 50.6% to 63.8%. The SrO modification lowers the amount of weakly adsorbed molecular oxygen species that could shift the reaction toward the deep oxidation, with the net consequence on CO<sub>x</sub> production.

In Table 2, the activities of some other group IA and IIA catalysts recently reported are presented. The various results indicated the



**Table 2**

Behaviors of some group IA and IIA catalysts during OMC reaction.

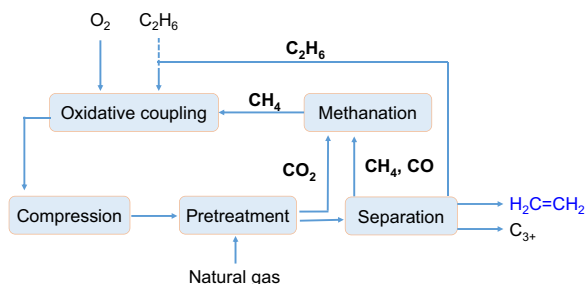
Catalyst	Reaction condition	Methane conversion, %	Ethylene/C <sub>2</sub> selectivity (S) OR yield (Y), %	CO <sub>x</sub> (x = 1, 2) selectivity/yield, %	Ref.
BaSrTiO <sub>3</sub>	1.5 g of catalyst, CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 40:20:40, 6000 h <sup>-1</sup> , 800 °C	47	14 (Y)	Not reported	[76]
4.49 wt.%Li/BaSrTiO <sub>3</sub>	1.5 g of catalyst, CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 40:20:40, 6000 h <sup>-1</sup> , 800 °C	37	22 (Y)	Not reported	[76]
5.25 wt.%Mg/BaSrTiO <sub>3</sub>	1.5 g of catalyst, CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 40:20:40, 6000 h <sup>-1</sup> , 800 °C	46.5	20 (Y)	Not reported	[76]
3.40 wt.%Na/BaSrTiO <sub>3</sub>	1.5 g of catalyst, CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 40:20:40, 6000 h <sup>-1</sup> , 800 °C	47	24 (Y)	Not reported	[76]
CaO powder	200 mg of catalyst, 800 °C; CH <sub>4</sub> , O <sub>2</sub> , and He flow of 8, 2, 10 mL/min, respectively	40	50 (S)	Not reported	[115]
30 wt.% CaO/SiO <sub>2</sub>	200 mg of catalyst, 800 °C; CH <sub>4</sub> , O <sub>2</sub> , and He flow of 8, 2, 10 mL/min, respectively	30	40 (S)	Not reported	[115]
LaInO <sub>3</sub>	800 °C, 0.7 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 5:1:20	15.4	53.6 (S)	Not reported	[116]
La <sub>0.9</sub> Ba <sub>0.1</sub> InO <sub>3-δ</sub>	800 °C, 0.7 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 5:1:20	21.7	59.1 (S)	Not reported	[116]
La <sub>0.6</sub> Ba <sub>0.4</sub> InO <sub>3-δ</sub>	800 °C, 0.7 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 5:1:20	21.4	61.1 (S)	Not reported	[116]
Sm <sub>2</sub> O <sub>3</sub> /MgO	0.4 g of catalyst, 700 °C, 2400 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> = 4:1	22	52 (S)	48	[117]
Li/Sm <sub>2</sub> O <sub>3</sub> /MgO	0.4 g of catalyst, 700 °C, 2400 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> = 4:1	24	64 (S)	36	[117]
1 wt.% Li/MgO	800 °C, 4500 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 4:2:4	38.05	35.19 (S)	Not reported	[118]
CaO/ZnO, Ca/Zn = 1.3	800 °C, 4500 h <sup>-1</sup> , CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> = 4:2:4	36.54	29.55 (S)	Not reported	[118]

catalyst composition and reaction conditions as critical factors for modifying the methane conversion and/or C<sub>2</sub>-selectivity/yield. According to Fakhroueian et al. [76], the incorporation of Na is more promising than incorporation of Li or Mg over BaSrTiO<sub>3</sub>. The Na containing catalyst produced the highest C<sub>2</sub>-yield of 24% compared to 20–22% with other catalysts. An et al. [115], demonstrated the incorporation of SiO<sub>2</sub> to yield a negative effect on the performance of CaO catalyst at 800 °C and methane/oxygen/nitrogen ratio of 8:2:10. Reaction with pure CaO powder yields 40% methane conversion and 50% selectivity to C<sub>2</sub>-species. However, when 30 wt.% CaO/SiO<sub>2</sub> was employed as catalyst, both the conversion and selectivity reduced to 30% and 40%, respectively. The decrease in concentration of CaO reduces the concentration of active basic sites for methane activation and consequently lowers the overall catalyst performance. This effect may increase the formation of CO<sub>x</sub> (i.e. CO and CO<sub>2</sub>) due to complete oxidation of hydrocarbon species. According to Tanaka et al. [116], incorporation of Ba into LaInO<sub>3</sub> can enhance its catalytic performance. Under the reaction conditions of 800 °C, 0.7 h<sup>-1</sup> and methane/oxygen/nitrogen ratio of 5:1:20, the parent LaInO<sub>3</sub> catalyst yields 15.4% methane conversion with 53.6% selectivity to C<sub>2</sub> species. When Ba was incorporated to form La<sub>0.9</sub>Ba<sub>0.1</sub>InO<sub>3-δ</sub>, both the conversion and selectivity increased to 21.7 and 59.1%, respectively. A similar trend could be observed when the parent catalyst was modified to La<sub>0.6</sub>Ba<sub>0.4</sub>InO<sub>3-δ</sub>. The conversion and selectivity increased to 21.4% and 61.6%, respectively. According to these results, replacing some La species with Ba provide an active surface suitable for the generation of methyl radicals, with enhanced possibility for conversion into ethane and ethylene. The work of Elkins et al. [117], demonstrated promotion with Li as an effective way of reducing the formation of CO<sub>x</sub>, with enhanced selectivity to ethylene/ethane (i.e. C<sub>2</sub>-species) over Sm<sub>2</sub>O<sub>3</sub>/MgO catalyst. For a reaction conducted at 700 °C and 2400 h<sup>-1</sup>, employing methane/oxygen ratio of 4:1, the parent Sm<sub>2</sub>O<sub>3</sub>/MgO catalyst yields 22% methane conversion and 52% and 48% selectivity to C<sub>2</sub>-species and CO<sub>x</sub>, respectively. However, incorporation of Li successfully raised the conversion to 24%, selectivity of C<sub>2</sub>-species to 64% and reduced the selectivity of CO<sub>x</sub> to 36%. Promotion with Li inhibits the possibility of complete oxidation of hydrocarbons (C<sub>2</sub><sup>+</sup> species) into CO and CO<sub>2</sub> and therefore lowers their selectivity. Raouf et al. [118], compared the activity of 1 wt.% Li/MgO and CaO/ZnO (Ca/Zn = 1.3) at 800 °C, 4500 h<sup>-1</sup> and methane/oxygen/nitrogen ratio of 4:2:4. Under these conditions, the former catalysts were more active. It produced 38.05% methane conversion and 35.19% selectivity of C<sub>2</sub>-species compared to the respective values of 36.54% and 29.55% obtained with the CaO/ZnO catalyst. Catalysts

based on Li/MgO are good candidates for the OMC reaction due to their associated basicity properties. However, appropriate reaction conditions must be carefully selected to achieve the desired activity, C<sub>2</sub>-selectivity and stability properties. According to Vatani et al. [119], important parameters such as space velocity and methane to oxygen ratio can also affect the activity of Li/MgO catalyst. When the reaction was conducted at 800 °C and methane/oxygen ratio of 2, increasing the space velocity from 2 to 45 h<sup>-1</sup> raises the methane conversion from 10% to 40%. The selectivity to ethylene also increased from 10% to 30%. However, lowering the reaction temperatures between 800 and 720 °C does not alter methane conversion, but the ethylene selectivity decreased with a decrease in temperature. On the other hand, varying the methane to oxygen ratio at 800 °C and 35 h<sup>-1</sup> alters the selectivity. When the ratio was 1, the ethylene selectivity was 30% but increased to 40% when the ratio was raised to 4. The trend was generally consistent with observations from studies conducted with related and other OMC catalysts [95,120–127].

### Prospects of nanowire catalysts

The various literature presented in this paper indicated that, although some recent improvements have been achieved in terms of enhancing methane conversion and ethylene selectivity by modifying compositional properties of catalysts and/or reaction conditions, researchers were unable develop suitable catalysts for the OMC reaction during the last three decades. Among the issues that remained partly resolved, lowering the reaction temperature, increasing ethylene yield and controlling catalyst lifetime are very crucial. However, recently Siluria Technologies patented a study which demonstrated nanowires-based biocatalysts as prospective catalysts to revolutionize the industry [128–131]. The nanowires were developed following the work of Dr. Angela Belcher of the MIT [132], who demonstrated nanowires based on Co<sub>3</sub>O<sub>4</sub> templated with virus as good materials for enhancing the capacity of Li<sup>+</sup> batteries. To prepare the catalysts, transition/non-transition metals or their oxide crystals were doped and carefully grown on biological substrates as templates. With the Siluria's nanowire catalysts, OMC can occur at much lower temperatures in the range of 200–300 °C. This lowers the energy requirement and in turn the exothermic heat produced during the reaction could be employed to drive the overall process. The nanowires could produce up to 90% methane conversion and similar selectivity to ethylene [128]. Fig. 10 represents a typical approach for the Siluria's OMC [133]. It could be seen that, the feedstock (i.e. natural gas) is first pre-treated to remove unwanted impurities that can interfere with the



**Fig. 10.** A typical operational scheme for OMC reaction using the Siluria's approach (Ref. [133]).

reaction of interest. Clean oxygen is also required for the OMC reaction. Ethane generated during the process can further be transformed into ethylene and  $C_3^+$  hydrocarbons, which are later separated at the separation units. The figure illustrated that, the Siluria's approach also encompassed compression and methanation units to ensure improved yield of ethylene and methane recyclization during the process.

Although natural gas is the main feedstock being considered currently, the re-ignited discovery and production of shale gas could shift the trend toward its valorization via the process. In this regard, the technology can benefit many global countries (i.e. both conventional natural gas and shale gas bearing countries). However, the variability of shale gas compositions from one field to another that may significantly differ from those of the conventional natural gas must be carefully considered [99,134,135]. The typical compositions of shale gas from Barnett field United States include 80–94% methane, 2–8% ethane/ethylene, 0–2% propane/propylene, 1–2% carbon dioxide and 1–8% nitrogen gas whereas the wells from Marcellus field usually contain <1% of nitrogen and carbon dioxide [136]. Wells from New Albany field could have up to 10% carbon dioxide with very little or no  $C_2$  and  $C_3$  compounds or nitrogen whereas wells from Antrim formations can possess nitrogen as high as 65% with <30% methane [137,138]. Some reservoirs in other parts of the world could also be rich in hydrogen sulfide or other impurities that must be removed prior to valorization [8,139–141]. Therefore, key important issues related to pipeline system, methane quality, environmental requirements and appropriate choice of pre-treatment conditions must be technically and economically considered. The available amine/glycol solutions methods for the removal of acidic gases (i.e. hydrogen sulfide and carbon dioxide) need to be upgraded in areas where the shale gas is in richer their compositions. Suitable technology that can sufficiently remove heavier hydrocarbon components that can undergo oxidation into CO and  $CO_2$  or hinder the overall progress of the OMC reaction due to carbonaceous deposits must be in place. This may require re-configuration of the distillation apparatus currently employed for the conventional natural gas before pipeline transportation. Other parameters to be considered include dehydration and cryogenic separation.

The Siluria's approach does not only limited to the modification of the oxide catalysts to the nanoscale but also appropriate choice of reaction parameters [142–144]. According to most of the literatures presented above, any commercial application will require large amount of catalyst and reactor volume. The Siluria's method targeted an improved gas hourly space velocity to orders of magnitude much higher than could be achieved with these previously evaluated bulk catalyst systems. Generally, temperatures below 600 °C and much lower than the 800–900 °C reported in the literature had been given preference, particularly due to the constraints associated with practical industrial reactors. It is clear that, most of these previous studies employed pressures below

≤1 atm, the Siluria's process emphasized on >1 atm pressure. Although the literature studies considered pure  $O_2$  as valuable reactant, at the industrial scale this will require an additional air separation unit, consequently elevating the process cost [142]. Siluria's process employed air directly as reactant. This in principle eliminates the incorporation of treatment plant and that, the nitrogen available can be beneficial in mitigating the exothermic temperature rise of the reactor during the reaction. Another key important feature of the Siluria's approach is the ability to send the unreacted ethane in the exit gas back to the reactor for oxidation to ethylene in a single step (Fig. 10). Higher  $n$ -alkanes that could be generated can also be transformed into high octane number gasoline by the process of hydroisomerization [145–151], catalysts for which the Siluria Technologies have already explored [152].

The nanowires and other nanoscale materials have therefore currently attracted good attention for evaluation as OMC catalysts [153–156], with most studies indicating the reaction can be achieved with enhanced ethylene yield at low temperatures. Noon et al. [157] conducted a study with nanofiber catalyst based on  $La_2O_3$  under variable reaction conditions. For reaction conducted using 20 mg catalyst and methane/oxygen ratio of 5, increasing the reaction temperature from 300 to 600 °C increases the methane conversion from 8% to 25%. The selectivity of  $C_2^+$  hydrocarbon species increased from 0% to 60%. An important issue here is the ability of the catalyst to be active at temperatures lower than 400 °C, a very difficult issue with bulk/powdered catalyst systems. When the methane/oxygen ratio was varied at 570 °C using 20 mg of catalyst and 80 mL/min total flow, the activity changed. Methane conversion was 32% at the ratio of 4 but decreased to 30% and 22% when the ratio was raised to 5 and 7, respectively. On the other hand, the selectivity increased from 54% when the ratio was 4–60 and 68% when the ratio reached 5 and 7, respectively.

Yunarti et al. [158] performed a study with nanowires based on  $TiO_2$  catalyst. Both unpromoted and metal-promoted  $TiO_2$  nanowires were evaluated in the temperature range of 750 to 850 °C. Without any modification, the  $TiO_2$  catalyst produced the highest conversion of 7% at 850 °C. Incorporation of V increased the conversion from 3% at 750 °C to 13% at 850 °C whereas the addition of Mn as promoter shifts the conversion from 14% at 750 °C to 20% at 850 °C. Highest methane conversions were achieved when Rh was employed as modifier. At 750 °C, the conversion over Rh- $TiO_2$  was 26% but increased to 31% when the temperature was raised to 850 °C. With regards to the  $C_2$ -selectivity, the Rh modified catalyst yields the worst selectivity of <2% at all temperatures. V- $TiO_2$  catalyst yields a maximum of 10% selectivity at 850 °C whereas Mn- $TiO_2$  yields 53% selectivity. According to these results, the yields of  $C_2$  species increased in the order Rh- $TiO_2$  < V- $TiO_2$  <  $TiO_2$  < Mn- $TiO_2$ . Modification with Mn produced the best yield of 14%. The low activities of pure  $TiO_2$  nanowires are in good agreement with results from previous studies [159,160].

Huang et al. [161] investigated the role of temperature on the activity of nanorods and nanoparticles based on  $La_2O_3$  catalyst. Increasing the temperature from 500 to 800 °C increased methane conversion from 5% to 31% for the nanoparticles whereas a stable conversion of 30% was obtained with the nanorods at all the temperatures (i.e. 450–800 °C). The results indicated the nanorods to successfully lower the temperature required to achieve good methane activation. Regarding the  $C_2$ -selectivity, nanorods produced 38% selectivity at 450 °C that only slightly reduced to 36% at 800 °C. The nanoparticles on the other hand yields no any selectivity to these species in the temperature range of 450–500 °C but produced 50% selectivity when the temperature reached 750 °C with a slight decrease to 48% at 800 °C. The enhanced low temperature catalytic activity of the nanorods was attributed to their large active surface area and associated surface

oxide species in addition to the well-defined structure of the surface. Previously, Lihua et al. [162] have reported a closer activity for the  $\text{La}_2\text{O}_3$  nanoparticles. The authors prepared a catalyst of 30–50 nm nanosize. When the catalyst was evaluated at 450 °C, 7.5 h<sup>-1</sup> and methane to oxygen ratio of 3, the methane conversion and C<sub>2</sub>-yield were 26.6% and 10.8%, respectively. Further evaluation of the catalyst for oxidative dehydrogenation of ethane to ethylene at 450 °C, 10 h<sup>-1</sup> and methane/oxygen/nitrogen ratio of 1:1:4, produced ethane conversion and ethylene yield of 49.1% and 25.9%, respectively.

Farsi et al. [163] compared the activity of powdered Li/MgO with that of corresponding nanocatalyst under constant conditions. For the powdered Li/MgO catalyst, increasing the reaction temperature from 700 to 800 °C at methane/oxygen ratio of 3, methane conversion increased from 21% to 26%. On the other hand, the nano Li/MgO catalyst produced an increased in conversion from 28% to 38%. Regarding the C<sub>2</sub>-selectivity, powdered Li/MgO yields 51.5% of these species at 700 °C and the selectivity increased to 56% at 800 °C. With the nanocatalyst, the selectivity increased from 60% at 70 °C to 64% at 800 °C. The nanocatalyst demonstrated stronger potentials to inhibit the total oxidation of hydrocarbons into CO<sub>x</sub> due to favorable structural effects. Al Mayman et al. [164] reported an ethylene selectivity of 100% with Li modified CeO<sub>2</sub>/ZnO nanocatalyst at 900 °C, methane to carbon dioxide ratio of 1 and total flow rate of 33 mL/min. However, the methane conversion was very low (i.e. 1%). Mahmoodi et al. [165] prepared W and Cr modified Na–Mn/SiO<sub>2</sub> nanocatalysts (12–92 nm) through impregnation method and evaluated their OMC activities at 775 °C using 1.8 g of catalyst and methane/oxygen/nitrogen ratio of 2:1:2. The W modified catalyst produced 46.1% methane conversion and 39.6% C<sub>2</sub>-selectivity whereas the Cr modified catalyst yields 40.1% and 11.5%, respectively. The authors attributed the enhanced activity of the W promoted catalyst to be associated tetrahedral structure of the WO<sub>4</sub><sup>2-</sup> species and the higher basicity properties.

## Conclusions

Oxidative methane coupling (OMC) reaction is an important natural gas valorization option currently being considered for upgrading shale gas, particularly due to the recent discoveries of huge profitable shale gas reserves and the associated increased in production in key global regions. However, developing the most appropriate commercially viable catalysts remained a crucial issue to researchers. Recent studies conducted with bulk/powdered pure or modified compounds of transition metals and of group IA and IIA elements indicated that methane conversion up to 50% could be achieved. However, the low yields of ethylene (10–25%) achieved with these catalysts indicated that further investigations are still necessary to meet the commercial requirement. Reaction with these catalysts was mainly dependent on the catalyst textural composition, preparation method, basicity and the ability to inhibit complete oxidation of hydrocarbons into CO<sub>x</sub> (i.e. CO and CO<sub>2</sub>) species. Parameters such as modification of catalyst with alkali metals, especially Li and Na, co-doping of oxide catalysts and catalyst preparation by different methods have all been demonstrated as good options for enhancing catalytic activities. But achieving ethylene yield of up to 40% is still very difficult. The most active among these catalyst systems are those that can produce a C<sub>2</sub> yield (i.e. combined ethylene and ethane yield) of ~35%. Similarly, the reaction must be conducted at high temperatures (750–900 °C) to obtain the optimal yields with these catalysts. It is particularly important to note that, many of the explored catalysts are associated with stability problems. They easily decomposed at the supposed working temperatures and became difficult to handle due to active sites decay with time. Therefore, further studies involving these catalyst systems should target how the

chemical compositions and synthetic procedures could be successfully modified to address the stated challenges. Catalyst stability at high reaction temperatures may be improved through the incorporation of appropriate dopants like CeO<sub>2</sub>, WO<sub>2</sub>, etc.

The recent discovery of bio-based nanowires by the Siluria Technologies, that can produce up to 90% yield of ethylene at temperatures below 600 °C, have open a door toward successful commercialization. Studies conducted with nanorods and nanowires following this development indicated that the reaction can be achieved at commercially affordable temperatures. However, effort to enhance ethylene yield by inhibiting complete hydrocarbons oxidation and enhancing catalyst lifetime is very critical. Other critical issues to be considered are the non-uniform growth and poor particles distribution of the nanowires. Therefore, various synthesis procedures like vapour phase growth, template-assisted synthesis and the template-free methods should be carefully evaluated to establish the most appropriate nanowires design method for the OMC application.

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