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Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review

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ABSTRACT

Despite its inherent constraints which hindered significant improvement in the process catalytically, the oxidative coupling of methane (OCM) remains an indispensable prospective approach for converting methane directly into vital chemicals such as ethylene. Recently, there is an upsurge in research effort towards better understanding of the oxidative coupling of methane process in terms of its mechanism, catalyst design and synthesis. This review discusses recent advances in crucial aspects related to the catalyst such as active sites, oxygen vacancy, acid–base property, surface oxide reducibility, oxide–support interaction, and prospects of nanowires with the aim to improve the performance of the OCM process.

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Introduction

With the enormous global natural gas reserve of around 208×10^{12} cubic feet [1,2] coupled with depletion of fossil fuel [3], researches exploring potential technologies for conversion of methane into more valuable chemicals are fast emerging [4–8]. Among all other methods, methane reforming into carbon monoxide and hydrogen has been the largest on industrial scale [9–12]. However, its high CO₂ emission [13] coupled with being strongly exothermic necessitates the search for other alternative processes involving direct methane conversion especially to higher hydrocarbons. Oxidative coupling of methane (OCM) is an indispensable approach which holds great prospect in converting methane directly into higher hydrocarbons especially ethylene in the presence of an oxidant [2,14]. Ethylene is known as a vital platform chemical for synthesis of most petrochemical products [15,16]. Even though the OCM reaction was reported as early as 1980s, the research output on the subject later declined after an upsurge due to some inherent constraints which hindered

significant improvement in the process catalytically, especially in terms of higher hydrocarbon yield [14].

The OCM reaction usually involves formation of methyl radicals (CH₃^{*}) via hydrogen abstraction from the methane by the active surface oxygen species available on the oxide catalyst surface [17,18]. The methyl radicals then couple in gaseous phase to form ethane (C₂H₆) which finally dehydrogenates to form the ethylene (C₂H₄) as depicted in Fig. 1. However, the OCM has long being constrained to low C₂ yield below economic viability, basically due to reasons which include: (1) Catalysts capable of activating CH₄ also activate the produced C₂H₆ in a similar rate, thus leading to generation of CO_x gases which are highly stable thermodynamically [19,20] (2) Refilling of generated vacant surface oxygen sites by the gas phase oxygen sometimes results in adsorbed oxygen species which facilitate CO_x formation as an unwanted scheme (3) Also, diffusion of the bulk lattice oxygen to the oxide surface is usually very slow and hence resulting in low overall activity especially in the absence of gas phase oxygen stream (4) The chances of methane combustion is usually high due to the high temperature requirement (above 800 °C) of the OCM reaction [21]. Detailed kinetic study revealed that the rate of formation of the CO_x increase with increase in partial pressure of methane and also partial pressure of oxygen [22].

The nature of oxidizing agent used could strongly influence the OCM performance [23,24], most probably due to the catalytic nature of the oxygen species formed during the catalyst

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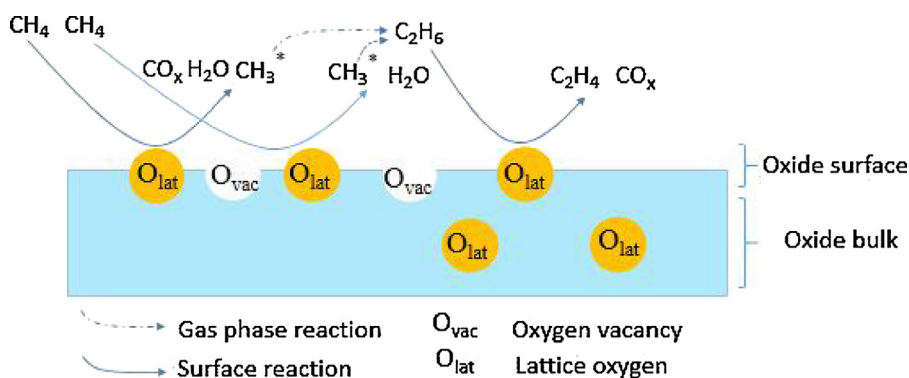


Fig. 1. Schematic representation of oxidative coupling of methane (OCM) reaction on metal oxide catalyst surface.

re-oxidation process [25,26]. Investigation with various catalyst systems revealed that nitrous oxide offered superior performances in terms of C_2 yield than molecular oxygen [26], even though the former is too expensive to be used on industrial scale [14]. In comparison to single-pass, multi-stage system via methane recycling along with ethane could also increase the commercial viability of the OCM process [27]. Besides, reactor configuration strongly contributes to the OCM performance [28–31]. Membrane reactors usually offer better C_2 selectivity by limiting the quantity of oxygen ion species available for reaction with the methane molecules via the selectively-conducting membranes [4,27,32]. However, unless operated at elevated temperature, the use of standard conducting oxides as membranes usually results in lower methane conversion in comparison to fixed bed reactors operated under molecular oxygen stream [4,27]. This is primarily due to the thickness of most of the oxides used which limits the rate of their oxygen ion conduction.

The use of an external power source [4] or regulating other parameters (such as methane to oxygen ratio, WHSV, temperature and sweep gas flow rate) to control the oxygen flux, use of dense fluorite-structured membrane [30] and the use of layered Ruddlesden–Popper mixed ionic/electronic oxides [33] could potentially improve the oxygen conduction and consequently the OCM performance. Notably, Othman et al. reported that an OCM reaction conducted in a novel microreactor composed of a hollow fibre membrane (made of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)) led to an excellent C_2 yield of 39% (highest reported so far in literature) at an approximate methane conversion of 50% [34]. They successfully in-situ deposited a nano-thick (300–500 nm) layer of $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) as functional catalytic substrate onto the hollow fibre surface via a sol–gel method. Obviously, uniform dispersion of the nano-sized BYS particles (which led to higher oxygen permeation rate and improved active site accessibility) and reduction of the residence time are the key variables behind the observed high OCM performance. Besides, Bhatia et al. have also reported an outstanding work on comparative performance of packed bed catalytic membrane reactor (PBCMR) with packed bed catalytic reactor (PBCR) and catalytic membrane reactor (CMR) [30]. At a temperature of 850 °C and GHSV of 23947 $cm^3/g\ h$, C_{2+} yields of around 30.4 and 34.7% was achieved with PBCR and CMR respectively. The CMR was composed of mixed ionic–electronic oxide conducting membrane (MIECM) coated internally with Na–W–Mn active catalyst.

Despite the recent outstanding C_2 yields, the membrane reactor still has other challenges that may impede on its stable performance [35]. These include chances of cracking and leakage due to difference in thermal expansion coefficient between the membranes and coated catalysts [30,35,36] or alteration of the catalyst properties due to solid state reaction with the membrane at high temperature [35,37]. Also, lack of large area of intimate

contact between the coated catalyst layer and the membrane may limit the flow of the generated O^{2-} ions. Conversely, even though the OCM performance for packed beds has long being constrained in getting to the commercially viable stage, most of the works reported on OCM largely employed the packed bed reactor due to its relatively less complex nature. Interestingly, a dual-reactor concept operated at the same pressure is reported to have an improved overall C_{2+} yield of 34% [38]. The second reactor hydrogenates the OCM-generated CO_x at a lower temperature to higher hydrocarbons [14] and its performance could be slightly improved (to C_{2+} yield of 38%) with removal of water from the inlet stream to the reactor [39].

Apart from the reaction-engineering approaches and integration of the OCM reaction with other processes, novel design of highly active and selective catalyst materials is also a vital aspect towards improving the overall OCM performance [32,34,35]. Consequently, many researchers are inspired to further investigate the key factors which play crucial role in determining the product selectivity catalytically. In recent times, fundamental experimental studies [18,40–42] and density function theory (DFT) computations [43–46] have provided spectacular insights into the OCM catalyst property–activity relationship and the reaction mechanism. Generally, active sites of catalysts usually facilitate chemical reactions via electronic interaction with the guest molecules and this greatly depends on the electronic arrangement of the catalyst material [47–49]. Conspicuously, the Schrödinger equation captures the quantum mechanical behaviour of the electrons and DFT methods provide approximate solution to the equation when the elemental composition and structure of the catalyst material is known [50,51].

Interestingly, many excellent reviews and viewpoints exist which discussed the OCM process specifically [27,29,52,53] or along with other methane conversion processes [2,4,6,11,13,14,54–56]. However, for the fact that in recent times, concerted research efforts have been made in further revealing the nature of active sites and other crucial aspects related to the OCM catalyst such as oxygen vacancy, acid–base property, surface oxide reducibility, and oxide-support interaction, the need to systematically and comprehensively discuss such advances is paramount. Thus, the present literature is hoped to contribute significantly in providing better insight into the design and development of efficient OCM catalyst.

Active sites

The active sites involved in the activation of the C–H bond of the methane molecules in OCM reaction are generally believed to be reactive oxygen species available on the oxide catalyst surface. However, different opinions were reported regarding the nature of these active sites possibly due to the presence of different kinds of oxygen species on the oxide surface and each may play a selective

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