Contents lists available at ScienceDirect



Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Review

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



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ARTICLE INFO

Article history: Received 10 October 2015 Received in revised form 2 March 2016 Accepted 17 March 2016 Available online 22 March 2016

Keywords: Shale gas Oxidative methane coupling Methane-to-ethylene Catalysts Nanowires

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 increased 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, electricity/power generation,

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http://dx.doi.org/10.1016/j.jiec.2016.03.027

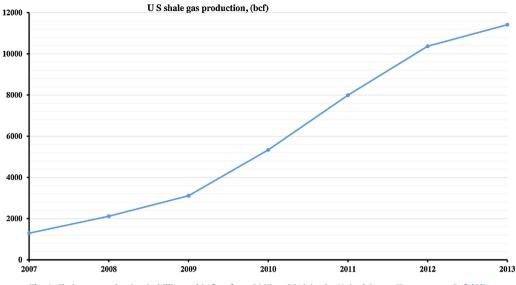


Fig. 1. Shale gas production in billion cubic feet from 2007 to 2013 in the United States (Data source: Ref. [9]).

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

Technically recoverable shale gas reserves, tcf

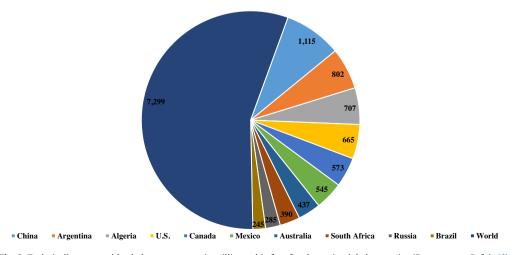


Fig. 2. Technically recoverable shale gas reserves in trillion cubic feet for the main global countries (Data source: Ref. [10]).

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