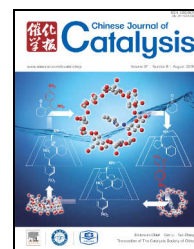


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## Review

# A review of the direct oxidation of methane to methanol



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## ABSTRACT

This article briefly reviewed the advances in the process of the direct oxidation of methane to methanol (DMTM) with both heterogeneous and homogeneous oxidation. Attention was paid to the conversion of methane by the heterogeneous oxidation process with various transition metal oxides. The most widely studied catalysts are based on molybdenum and iron. For the homogeneous gas phase oxidation, several process control parameters were discussed. Reactor design has the most crucial role in determining its commercialization. Compared to the above two systems, aqueous homogenous oxidation is an efficient route to get a higher yield of methanol. However, the corrosive medium in this method and its serious environmental pollution hinder its widespread use. The key challenge to the industrial application is to find a green medium and highly efficient catalysts.

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## 1. Introduction

Natural gas has proven reserves far more than that of crude oil. It consists of 90% methane and is a promising energy resource to substitute for crude oil. Much attention has been paid to the activation and functionalization of methane to useful hydrocarbons and oxygenated products. One of the most challenging processes of high industrial importance is the conversion of natural gas or methane to methanol, which is an important intermediate source of energy in our daily lives. For example, methanol is an important fuel for heating, automobiles and as the replacement of MTBE (methyl *tert*-butyl ether) as an additive in petrol.

Conventionally, an indirect route for the conversion of natural gas to methanol is used. The reactions are: (1) intermedi-

ate production of synthesis gas by steam reforming, and (2) catalytic conversion of synthesis gas to methanol. However, the production of syngas is an energy-intensive process, which is operated at 65% thermodynamic efficiency between 800–1000 °C and more than 25% of the feed (natural gas) has to be burned to provide the heat of reaction. Hence, from the viewpoint of sustainable development, the direct conversion of methane to methanol is a desired alternative to the current technology [1]. There are some promising areas for the application of the direct partial oxidation of hydrocarbon gases, which is displayed in Fig. 1. [2]. In spite of the fact that there are no actual plants yet for the process of direct methane to methanol (DMTM), previous experimental and theoretical works have demonstrated the feasibility of this route [3]. Here, we assess the various methods and catalysts in different systems for the

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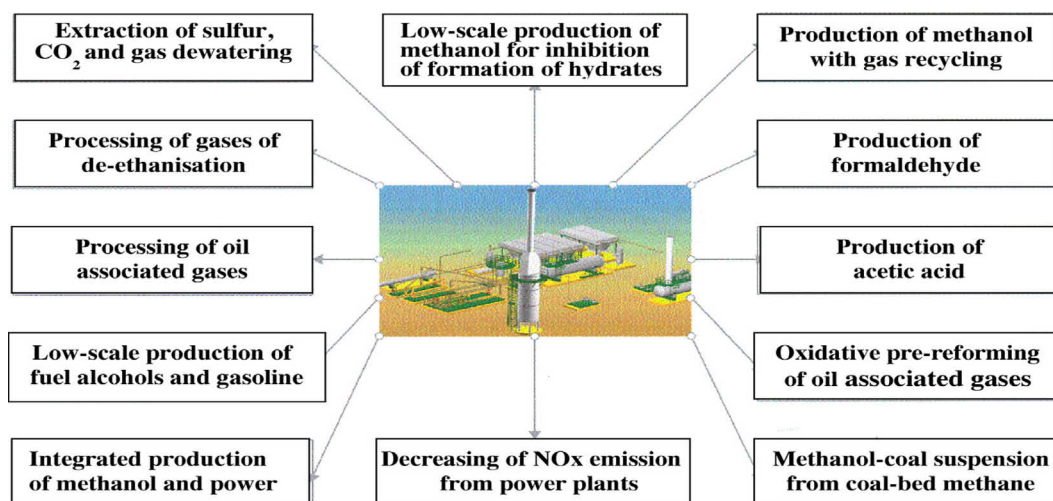


Fig. 1. Promising areas for the application of the direct partial oxidation of hydrocarbon gases. Reprinted with permission from Ref. [2]. Copyright 2007, Elsevier.

DMTM, and provide highlights on the approaches to overcome existing problems to realize industrial utilization of DMTM.

## 2. Catalytic oxidation of methane to methanol over heterogeneous catalysts

In the last century, many publications in this field have discussed the partial oxidation of methane at high temperature over transition metal oxides catalysts. The most widely studied catalysts were those based on molybdenum trioxide and iron compounds.

### 2.1. Molybdenum-based catalysts

Atroschenko et al. [4] first investigated various metal oxides for the partial oxidation of methane, and reported that MoO<sub>3</sub> was one of the best catalysts at elevated temperature and pressure. The authors also found that the successive oxidation of methanol was difficult.

One of the earliest patents was claimed by Dowden and Walker [5], who developed a series of multicomponent oxides based on molybdenum. They stated that the most active catalyst was Fe<sub>2</sub>O<sub>3</sub>(MoO<sub>3</sub>)<sub>3</sub>, which yielded 869 g kg<sup>-1</sup> h<sup>-1</sup> of methanol.

In 1982, Liu et al. [6] studied the kinetics and mechanism of the partial oxidation of methane using N<sub>2</sub>O and MoO<sub>3</sub>/SiO<sub>2</sub> catalysts. They obtained a combined selectivity of 84.6% towards methanol and formaldehyde. Their results indicated a rate law of the form,  $d[\text{CH}_4]/dt = -k[\text{N}_2\text{O}]^1[\text{CH}_4]^0$ . These researchers also found that it was the more reactive O<sup>-</sup> species that was responsible for initiating the selective oxidation cycle, which was formed by the interaction of N<sub>2</sub>O with surface MO (V) species.

Liu et al. [7] and Sugino et al. [8] successively reported that the addition of steam to the system with a MoO<sub>3</sub>/SiO<sub>2</sub> catalyst increased the selectivity to oxygenates by inhibiting further oxidation due to the formation of H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>, but most of the product was formaldehyde.

Zhen et al. [9] compared V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> to MoO<sub>3</sub>/SiO<sub>2</sub> catalysts

for the partial oxidation of methane, and concluded that although the former catalyst was more active for methanol production, its product selectivity was generally poorer. The maximum conversion to methanol was only 0.2% at 460 °C.

Spencer [10] carried out methane partial oxidation using molecular oxygen over a MoO<sub>3</sub>/SiO<sub>2</sub> catalyst. However, only trace amounts of CH<sub>3</sub>OH was produced. Similar results were obtained by others [11–13], regardless of whether dopants were added to the catalyst.

Later researchers focused on finding more effective support which can replace SiO<sub>2</sub> to increase the selectivity to methanol. Taylor et al. [14] investigated the oxidation of methane over a MoO<sub>3</sub> catalyst on different supports and found that Ga<sub>2</sub>O<sub>3</sub> was the best support of MoO<sub>3</sub> with the highest selectivity (22%) to methanol. They suggested that a cooperative effect between MoO<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> played a crucial role in increasing the yield of methanol when compared to the other complex metal oxides.

### 2.2. Iron-based catalysts

Otsuka and Wang [15] studied the reaction mechanism for the partial oxidation of methane over an iron sodalite catalyst (Fig. 2). From considering the mechanism of methane monooxygenase for alkane oxidation, Lyons and co-workers [16,17] designed an iron sodalite-based catalyst that showed 70% selectivity to methanol with 5.7% methane conversion at 416 °C and 5.5 MPa using a 3:1 methane-air mixture. They also discussed several similar types of catalysts, and suggested that altering the redox potential of the Fe(II) species can eliminate the requirement of electrons and protons in the biological systems to increase methanol selectivity by mimicking the μ-oxo-bridged binuclear iron centers. Through a combined theoretical and experimental study, Betteridge et al. [3] observed that in a simple flow reactor, there was only a small region where the selectivity was enhanced in the presence of iron sodalite.

Otsuka and Hatano [18] studied the kinetics of the partial oxidation of methane over a Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> catalyst. They ob-

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