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Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review

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ABSTRACT

In the current era of energy crises, alternative feedstock such as methanol are commonly used as fuels and solvents in various industries. Methanol is commonly produced from non-renewable sources. Recently, sustainable methanol synthesis via innovative and efficient catalytic processes has drawn a lot of attention and research is currently aimed at finding a suitable catalyst for optimized production at commercial scale. Nowadays, one of the main interests is catalytic synthesis of methanol from CO_2. This work presents a critical review on innovative catalysts for methanol synthesis, research progress for their development and their use in the catalytic process. It also provides an overview on recent development in methanol synthesis from syngas, CO_2 hydrogenation and photo-catalytic reduction of CO_2. The use of various reactors, the influence of preparation method, support, promoter, different type of catalysts used, their properties and performance during methanol synthesis are also thoroughly reviewed.

Contents

1. Introduction

Methanol is a widely used and globally distributed product with number of industrial applications. It is also very important

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due to the current depletion of fossil fuel resources. It is considered to be an ideal alternative fuel due to fast dismissing oil and gas resources [1]. In chemical industry, commercial uses of methanol include the production of formaldehyde, aromatics, ethylene, methyl tertiary butyl ether (MTBE), acetic acid and other chemicals [2]. There is also a growing demand for methanol in fuel application such as production of dimethyl carbonate (DMC), biodiesel production, the direct blending into gasoline and it could provide conventional energy storage for fuel cell applications due to its cleaner emissions as compare to fossil fuel resources [3]. Figs. 1 and 2 illustrate data regarding the worldwide methanol consumption and its industrial demand.

The commercial production of methanol is mainly from fossil fuel based syngas that generally contains CO and H_2 with small traces of CO_2. Meantime, the high temperature and pressure requirement for this process has a serious impact on the environment [5]. Over the past decades, researchers have been focusing on the potential of CO_2 hydrogenation to produce methanol. CO_2 is an important greenhouse gas that is the main causal agent for climate change and global warming [6]. In this regard, its utilization is an attractive way to reduce CO_2 concentration in the atmosphere [7].

In addition, according to the Kyoto Protocol, some industrialized countries and European community are committed to reduce their greenhouse gas emissions [8]. The emission level must be reduced by 5% below their emission level in 1990 during a five year period (2008–2012). Three market-based mechanisms were offered to help in achieving the targets i.e. (i) emission trading known as “the carbon market”, (ii) clean development mechanism (CDM) and (iii) joint implementation (JI) [9]. Even though carbon dioxide is readily available, it is thermodynamically stable, coupled with its standard free energy of formation ($\Delta G^{\circ} = -394.359$ kJ/mol) [10]. Large energy source is required in reduction/splitting process. It is also well establish that the methanol can be readily produced through CO and CO_2 hydrogenation [11].

Recently, the main interest in methanol synthesis is to develop highly efficient and innovative catalysts. In this regard, a number of investigations have been conducted to develop catalysts with large surface area, high active site dispersion and smaller particle size in order to increase activity and selectivity. Among these, Cu-based catalysts have been given great attention. A work by Zhang et al. [12] showed that the addition of metal ions onto Cu-based catalyst increased the activity and stability of the catalysts. Hong [13] found that the properties and performance of Cu-based catalyst could be adjusted by varying preparation parameters and methods. In the work of Robinson and Moi [14], it was proven that besides the active site on which the reaction occurred, type and structure of the support also had an influence on the methanol synthesis. Even with all these findings, there is still a need for enhancement of Cu-based catalyst and also the preparation of new catalysts to address drawbacks of currently available catalysts. Ideal catalyst properties include a primary component that shows good selectivity and activity towards the desired product, a support that not only provides good configuration and stability but also has some modulating interaction between the primary component and promoter, and a promoter that further enhances the catalyst ability. All these objectives could be achieved by using a robust preparation method.

Similarly, another environmentally friendly way to produce methanol that has been gaining more attention is photocatalytic reduction of CO_2 with water in the presence of light irradiation. An attractive feature of photocatalysis is that it occurs under relatively mild conditions with readily available and relatively cheap source of reactant. By using suitable semiconductor material as a catalyst, the absorption of light energy generates electron and holes needed for the reduction reaction. In this case, CO_2 can be reduced to useful chemicals such as formic acid, formaldehyde, methane and methanol [15]. To date, a number of catalysts have been investigated for photocatalysis such as ZnS, CdS, ZrO_2, TiO_2, MgO and ZnO [16]. Among these catalysts, TiO_2 has been widely used due to its high catalytic activity [17] and comparable band energy (3.2 eV) to the reduction potential of CO_2 [18].

Even though TiO_2 is a good catalyst for methanol production, one of the most challenging tasks is to have enhanced efficiency in the photochemical process. Methanol yield from this process is still competitive to the yield by syngas or hydrogenation process. Looking at the thermodynamics of the reaction, 228 kJ of energy is required to convert one mole of CO_2 to methanol with six electrons to convert C^{4+} in CO_2 to C^{2-} in methanol. In addition, with poor visible light response from TiO_2, significant improvement is necessary in order to upgrade this process to an industrial scale. One of the prominent ways is by modifying TiO_2 catalyst with other metals and semiconductors. Since this is still a new research area, there are only few reported studies that involve modification of TiO_2 catalyst. Further innovation in TiO_2 catalysts as well as the use of other semiconductor is vital in enhancing the efficiency of the process.

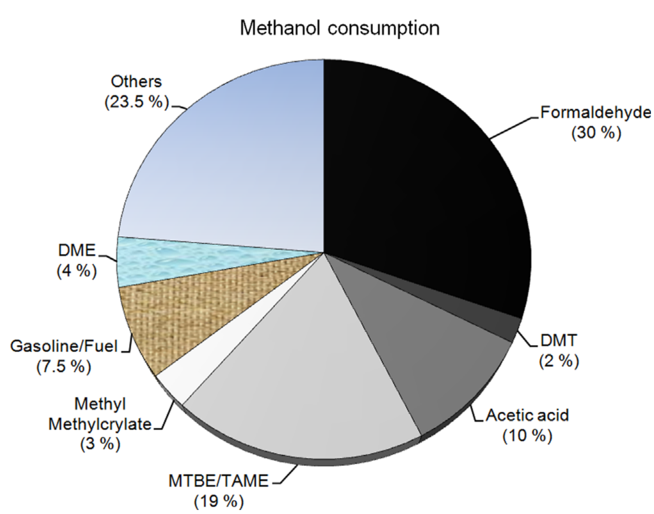

Fig. 1. Methanol consuming industries [4].

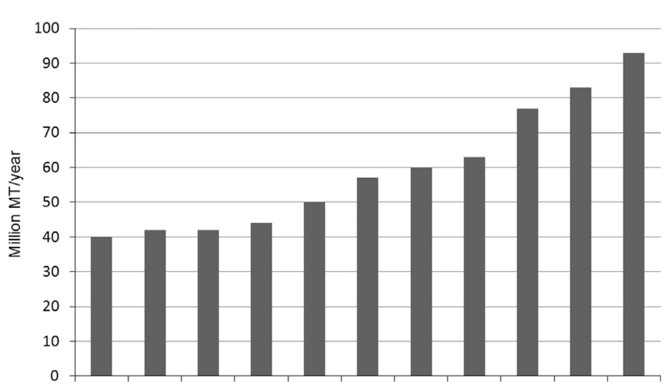

Fig. 2. Trend in methanol demand for a 10 year period [3].

2. Methanol synthesis through CO_2 hydrogenation

2.1. Effect of catalyst preparation method

Currently, the synthesis of methanol is rather promising due to its dramatic economic values and significance for use as alternative