One step catalytic oxidation process of methane to methanol at low reaction temperature: A Brief Review

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Abstract. Methanol has good combustion properties, so it is projected to be a profitable alternative for future fuel. Single step oxidation of methane to methanol can be chosen as an alternative process, because this process is more economical than the conventional two-step process. Although in the thermodynamic analysis shows that partial oxidation of methane to methanol can be carried out at room temperature, but the low selectivity and side reactions are still to be a challenge. To getting the methanol as a product or intermediate, it is important to determine the suitable materials that can activate methane in an efficient way at low temperatures. This is difficult because the C-H bond in CH₄ has the highest bond energy (104 kcal / mol) among other organic compounds. Some oxide and metal oxide surfaces can dissociate CH₄ at room temperature, which opens the possibility for a direct conversion methane to methanol. And the addition of water to the system causes a big change in the selectivity of methane activation yielding which only produces adsorbed CHx fragments. In this paper we will review one step catalytic oxidation process basically, solid heterogeneous catalytic oxidation of methane, and some suitable catalysts and materials that can support the reaction of the conversion of methane into methanol.

1. Introduction

A significant part of the increase on greenhouse gas (GHG) emissions is due to methane. Methane, CH₄, is the second most abundant GHG. Global averages of the greenhouse gases concentrations in sequence from the greatest are carbon dioxide, methane, nitrous oxide, CFCs-12 and CFCs-11 [1]. Methane has a tendency to trap heat and absorb infrared radiation (IR), which causes on increasing the earth’s temperature and affecting the climate. But, in the other hand, methane has many advantages, such as the cleanest fossil fuel and as an attractive substitute for the crude oil in chemical industry. Methane has also advantage as a fuel source because of its high calorific properties. The current challenge is convert methane to be more suitable energy carriers, useful products, and easily transportable chemicals (liquid), such as converting methane to methanol. This conversion process is one of the many ways to reduce GHG emissions and to prevent climate change. Methanol is the simplest member of alcohols. Methanol, the chemical name of CH₃OH, has good combustion properties, so it is projected to be a profitable alternative for future fuel, and it appears to be the best candidate to replacing petroleum-based fuels in the long term [2-4]. In addition, methanol is also used in the industry as a solvent, cosolvent, fuel additive, and as a raw material for the production of...
inorganic and organic bulk chemicals such as acetic acid, methyl ter butyl ether (MTBE), methyl and vinyl acetates, and others [1, 5, 6, 7].

The process conversion for methanol manufacturing are still being developed by many researchers in the world. Methanol can be produced from methane via indirect conversion or direct conversion method with many supporting technologies, such as via plasma technology, photo-catalysts technology, supercritical water technology, catalytic process, and others [1]. Plasma technology includes some components, such as positive ions, negative ions, electrons, and neutral species. Photocatalyst technology is one of the green alternative technique for methane conversion under mild conditions, by using a suitable catalyst and light [8]. Supercritical water oxidation occurs at high temperatur and high pressure above thermodynamic critical point of the mixture which will destruct methane [1]. Savage [11] reviewed in a paper that partial oxidation methane to methanol via supercritical water technology does not look to be worthy route, because the highest methanol yield obtained is only about 1%.

Indirect pathway for conversion methane to methanol is well-known as two step conversion method and widely used in chemical industry. Its reaction is devided to three steps (illustration can be seen at Fig.1). The first step is produce synthesis gas by steam reforming of methane.The second is followed by high pressure catalytic conversion syngas to methanol using Cu-Zn-O based catalyst such as Cu/ZnO/Al$_2$O$_3$ [18]. And in the third step, the crude methanol is separated from the unconverted synthesis gas and purified, while the unconverted syngas is recycled [2, 9,10]. This process is operated in elevated temperature up to 1000 ºC and elevated pressure, automatically needs high energy. The synthesis gas generation is the most expensive step in many processes, about 60% of the production cost [7, 19]. Whereas, direct conversion methane to methanol is more economical than convensional two step process. Therefore, direct routes involving the partial oxidation methane to methanol, or one step catalytic oxidation, can be chosen as an alternative process, than the conventional two-step process.

![Fig. 1 Block flow diagram of conversion methane to methanol](image)

The disadvantage of direct methane to methanol is the difficulty to reach high selectivity of methanol and conversion of methane. It is because methane has the high C-H bonding energy, 104 kcal/mol, which causes difficult in activating the methane C-H bond but it can be overcome by using extreme conditions or using suitable catalyst [5, 12-14]. Besides that, the dissociation energy of the C-H bond of methanol is approximately 47 kJ/mol lower than methane, thus methanol is particularly susceptible to deep oxidation to be carbon dioxide. Thus, an effective catalyst can facilitate the methane activation at low temperature and simultaneously prevent further methanol oxidation to carbon oxides [5]. Therefore, the catalytic process is appropriate supporting method for conversion methane to methanol selectively, either via indirect or direct conversion methane to methanol [12].
2. Basic one step oxidation process of methane to methanol

Methanol can be produced by the direct partial oxidation of methane to methanol, or can be called one step oxidation process of methane to methanol. This process conversion involves the reaction of methane and oxidant or using an oxygen gas (O$_2$) appears to be an ideal process. One step oxidation process of methane to methanol is challenging because the reaction takes place all the way continuously to yield CO and or CO$_2$ as the side reaction [12]. The following is the reaction that occur in the process :

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2} \text{O}_2 &\rightarrow \text{CH}_3\text{OH} \quad \text{(1)} \\
\text{CH}_4 + \frac{1}{2} \text{O}_2 &\rightarrow \text{CO} + 2\text{H}_2 \quad \text{(2)}
\end{align*}
\]

Reaction (1) is the main reaction, while reaction (2) is the side reaction. In thermodynamic, both of them are exothermic reactions and include spontaneous reactions at room temperature. At temperature above 600 K, reaction (2) becomes the preferred route from thermodynamic viewpoint because Gibbs free energy of reaction (2) lower than reaction (1) [2]. To reach methanol as a product, it is important to find the suitable materials that can activate methane at low temperature (below 500 K).

There are 3 main obstacles in the route of direct partial oxidation methane to methanol as follows:

1. Activating C-H bonding of methane is difficult. It happens because methane is stable hydrocarbon and has high dissociation energy of C-H bond, 440 kJ/mol. It needs extreme conditions to can activate the methane well.

2. Thermodynamically difficult to maintain and isolate methanol as product, especially at temperature above 600 K (2). In addition, the dissociation energy of C-H bond of methane (439 kJ/mol) is higher than in methanol (402 kJ/mol). Thus, methanol is susceptible to further oxidation to CO and/or CO$_2$. As a result, methanol will work better to be activated and oxidized than methane itself.

3. Methanol more sensitive to be absorbed than methane on the surface of catalyst or reactor wall. Methanol is a polar compound which contains an oxygen atom. Whereas, methane is an unpolar compound.

Obtaining high selectivity and high conversion need more struggle. The more reasonable methanol yields obtained suggests that it is possible to achieve methane conversion and methanol selectivity if methanol can be protected from further oxidation.

3. Simpled thermodynamic analysis of reaction of partial oxidation methane to methanol

| Table 1. The Gibbs free energies (kJ/mol) of the reaction in various temperature (K) [15] |
|---|---|---|---|---|---|---|
| No | Reactions | ΔGr (kJ/mol) | 298 | 650 | 700 | 750 | 800 | 1000 |
| 1 | CH$_4$ + 1/2 O$_2$ → CH$_3$OH | -111 | -93 | -91 | -88 | -86 | -76 |
| 2 | CH$_4$ + 1/2 O$_2$ → CO + 2H$_2$ | -86 | -152 | -162 | -172 | -182 | -222 |

| Table 2. Enthalpy of the reaction at 298 K [16] |
|---|---|---|
| No | Reactions | ΔHr 298 (kJ/mol) |
| 1 | CH$_4$ + 1/2 O$_2$ → CH$_3$OH | -126.32 |
| 2 | CH$_4$ + 1/2 O$_2$ → CO + 2H$_2$ | -35.36 |
Gibbs energy of formation is important in analysis of chemical reactions, which is used to determine the change of gibbs energy for the reaction at the certain temperature. The change is important because the reaction is related to its chemical equilibrium. If the change in gibbs free energy of the reaction is negative value, the thermodynamic for the reaction is favorable (spontan reaction). But, if the change in gibbs free energy of the reaction is highly positive value, the thermodynamic for the reaction is not favorable [16].

Based on table 1 above, in reaction (1) the gibbs free energies of partial oxidation methane to methanol is negative value, its mean that partial oxidation methane with oxygen can be carried out at low temperature from thermodynamic viewpoint. Equilibrium conversion can be calculated from gibbs free energy above, and the highest equilibrium conversion is obtained about 33% at 298 K, with the maximum conversion procured is about 5% [2].

Based on table 2 above, in reaction (1) the enthalpy of the oxidation reaction methane to methanol at 298 K is so exothermic, -126.32 kJ/mol, whereas the entalphy value of side reaction (2) is -35.36 kJ/mol. This is challenging and tends to produce oxygenated CO2 rather than methanol [17].

4. Catalytic partial oxidation methane to methanol using heterogeneous catalysts
Partial oxidation methane to methanol is challenging reaction because significantly different reactivities of methane and methanol [12, 18]. Partial oxidation methane to methanol is possible in thermodynamic point of view, but it is difficult or even impossible to avoid overoxidaton of methane because methanol is likely undergo oxidation in kinetic point of view. To get high selectivity of methanol, the reaction should be stopped in the formation methanol stage to avoid of the further oxidation into formic acid or CO and CO2 [12, 20, 21]. The recent years of research on the partial catalytic conversion of methane to methanol have shown that a higher conversion is related with a very low methanol yields, which results from further oxidation of this reactive molecule. Indeed, an example of a continuous process capable of simultaneously achieving high methane conversion and high methanol selectivity has yet to be developed.

The use of catalyst in an exothermic equilibrium reaction allows the reaction to be carried out at a lower temperature, which without the catalyst will be hindered by the kinetics. Thus, the use of a catalyst allows the reaction to be realized under conditions where thermodynamics is preferred [22].
Some researchers believe that successful process of direct methane to methanol will need the use of a very selective catalyst for C-H activation. The challenge for this process is to develop selection catalyst, which selectively direct methane to methanol. The catalysts that are often studied are those based on iron (Fe), Copper (Cu), Cobalt (Co), Zinc (Zn), and Nickel (Ni), Platinum (Pt) compounds, or combination of metals or with zeolite catalyst (ZSM-5, MOR, Y, X, CHA) [17, 23-28].

4.1. Copper-exchanged Zeolite
The advantage using of copper-based catalyst on partial oxidation methane into methanol is the ability to form active spesies without using high temperature at initial oxidation step, which is usual needed for iron and copper based catalyst. Framework of bound Zn²⁺ cations are belived to active C-H bond in methane [7].

4.2. Iron-exchanged Zeolite
This indicates that these catalysts are able to activate hydrocarbons and form active oxygen species in such a way that complete oxidation of the reactants towards carbon dioxide and water is prevented. The use of N₂O as an oxidant was essential and claimed to lead to a special type of reactive surface oxygen species, often called a-oxygen. The addition of O₂ and CH₄ respectively on the zeolite catalyst containing Cu and Fe species produced methanol with increased selectivity [17].
5. Suitable supporting materials for direct methane oxidation to methanol

Despite many claims in the literature regarding the beneficial effects of using a catalyst, it does not appear to offer a significant yield advantage [4, 14]. It appears that the role of catalysis is primarily to reduce the severity of process conditions. The partial oxidation of methane to methanol is more simply performed as a gas phase free radical process, which avoids gas scavenging to remove potential catalyst toxins.

The free radical partial oxidation of methane to methanol is less affected by the presence of hydrogen sulfide or other contaminants that may be present in natural sources of methane, such as natural gas. The reaction engineering strategy used to maximize the selectivity of methanol during the oxidation phase of methane gas is to limit single-path conversions. The ability to selectively convert methane to methanol stems from its capacity to stabilize intermediate species, such as methoxy, and thus protect it from excess oxidation. For copper zeolites, the copper must be activated by an oxidant, to make one or more active sites. These sites in turn serve to activate the C-H bond (at relatively low temperatures, usually between 423 K and 473 K) and then stabilize the methoxy species so that they are derived from further oxidation.

Instead of using a strong oxidant like O$_2$, water was employed as a soft oxidizing agent. In the presence of water, direct conversion of CH$_4$ into methanol with high selectivity (∼97%) was accomplished over a copper-containing zeolite at 200 °C. Moreover, Zuo et al. reported that a CeO$_2$/Cu$_2$O/Cu(111) film can activate methane at room temperature with the addition of water [14, 17].

6. Conclusion

There is a steady increase of public interest in the production of methane into methanol. One step conversion methane to methanol is one of the solutions to overcome the problems of expensive methanol production. Based on thermodynamic point of view, direct production methane to methanol at low temperature (273 K) is favorable reaction. But in some of studies show that direct reaction of methane to methanol at low temperature is obtained low conversion and low selectivity, therefore these reactions need the suitable catalyst and supporting materials.

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