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Review

Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies

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ABSTRACT

Methanol demand is continuously increasing in the chemical and energy industries. It is commercially produced from synthesis gas ($CO + CO_2 + H_2$) using $CuO/ZnO/Al_2O_3$ catalysts. Today, much effort is being put on the development of technologies for its production from carbon dioxide (CO_2). In this way, the Greenhouse effect may be mitigated. Over the years, several useful works on CO_2 hydrogenation to methanol have been reported in the literature. In this article, we present a comprehensive overview of all the recent studies published during the past decade. Various aspects on this reaction system (such as thermodynamic considerations, innovations in catalysts, influences of reaction variables, overall catalyst performance, reaction mechanism and kinetics, and recent technological advances) are described in detail. The major challenges confronting methanol production from CO_2 are considered. By now, such a discussion is still missing, and we intend to close this gap in this paper.

Keywords: Methanol; Syngas; Carbon dioxide; Carbon Monoxide; Hydrogenation; Cu/ZnO Catalyst; Pd Catalyst

Contents

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1. Introduction

Methanol is a primary liquid petrochemical which is of considerable importance in the chemical and energy industries. This large-volume product is in big demand, due to the ease in its storage and transportation. For example, it was anticipated that global methanol consumption will reach 58.6 MMT by 2012 (Centi and Perathoner, 2009). Methanol is commonly used as solvent and feedstock for the production of chemicals (such as formaldehyde, acetic acid, methyl methacrylate, dimethyl terephthalate, methylamines and chloromethanes) and fuel additives (such as methyl tertiary butyl ether and fatty acid methyl esters) (Ortelli et al., 2001). Light olefins such as ethylene and propylene, which can be used for manufacturing polymers and hydrocarbon fuels, are produced using the methanol-to-olefins process (Pop et al., 2004). Dimethyl carbonate, which is a useful intermediate for derivatives used in polycarbonates and polyurethanes, is synthesized from methanol in supercritical CO_2 (Ballivet-Tkatchenko et al., 2006). Methanol is a liquid energy-carrier suitable for transportation applications. It is an excellent alternative fuel, and it can also be blended with gasoline (Olah, 2005); moreover, it can be used in fuel cells, too (Palo et al., 2007).

Methanol is commercially produced from natural gas through a syngas route. Steam methane reforming produces a mixture of CO, CO_2 and H_2 according to Eqs. (1) and (2). Syngas is then converted to methanol in the ranges of temperature, 250–300 °C, and pressure, 5–10 MPa, using $CuO/ZnO/Al_2O_3$ catalyst (see Eq. (3)).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{25^\circ C} = 206\,\text{kJ/mol} \tag{1}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_{25^\circ C} = 165\,\text{kJ/mol} \tag{2}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{25^\circ C} = -49.5\,\text{kJ/mol} \tag{3}$$

Today, CO_2 is added up to 30% of the total carbon in syngas (Aresta and Dibenedetto, 2007). The addition of CO_2 in the CO/H_2 feed significantly improves the methanol yield and the energy balance. CO_2 is directly converted to methanol without a preliminary reduction to CO (Saito et al., 1996). To facilitate methanol synthesis, the CO in syngas is converted to CO_2 through the water-gas shift (WGS) reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{25^\circ C} = -41\,\text{kJ/mol} \tag{4}$$

Reactions represented by Eqs. (3) and (4) are exothermic. The overall reaction for methanol synthesis is given by the sum of these reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H_{25^\circ C} = -90.5\,\text{kJ/mol} \tag{5}$$

The theoretical single-pass CO conversion is limited to ~20% under commercial operating conditions (Strelzoff, 1970; von der Decken et al., 1987). Today, this process is well established and several companies such as Lurgi, Topsoe and Mitsubishi offer commercial technology solutions.

2. Methanol from catalytic hydrogenation of CO_2

Much effort is now being put on CO_2 conversion to methanol (see Eq. (3)). This method is a useful strategy of CO_2 utilization and a practical approach to sustainable development (Song, 2006). It is technically competitive with the industrial production of methanol from syngas (Aresta and Dibenedetto, 2007). The production of methanol and its derivatives by alternative routes and their use as fuels and chemicals is the core of the methanol economy, a concept earlier proposed by Olah and co-workers (see Olah, 2005; Olah et al., 2009a,b, 2011). In this conception, CO_2 is captured from any natural or industrial source, human activities or air by absorption and chemically transformed into methanol, dimethyl ether and varied products including synthetic hydrocarbons. According to Olah (2005), methanol production from CO_2 is advantageous owing to the usage of non-fossil fuel sources (unlike syngas), avoidance of CO_2 sequestration (which is expensive) and the opportunity for mitigation of the Greenhouse effect (by effective recycling of CO_2). Olah et al. (2009a) emphasized that the chemical recycling of CO_2 to methanol (and dimethyl ether) provides a renewable, carbon-neutral, unlimited source for efficient transportation fuels, for storing and transporting energy, as well as convenient feedstock for producing ethylene and propylene and from them, synthetic hydrocarbons and their products. Thus, it essentially substitutes petroleum oil and natural gas. It allows the lasting use of carbon-containing fuels and materials and avoids excessive CO_2 emissions causing global warming (Olah et al., 2009b).

The methanol economy concept is based on the chemical anthropogenic carbon cycle proposed by Olah et al. (2011). It combines carbon capture and storage with chemical recycling. While renewable feedstock such as water and CO_2 are available in plenty, the energy required for the synthetic carbon cycle can come from any alternative energy source such as solar, wind, geothermal, and nuclear energy. According to Olah et al. (2011), this cycle supplements the natural carbon cycle and offers a way of assuring a sustainable future for humankind when fossil fuels become scarce.

Interestingly, CO_2 is non-toxic, non-corrosive and non-flammable and it can be easily stored in liquid form under mild pressure. Therefore, the problem of process safety does not appear in the case of CO_2 application. Besides, the process can be easily integrated in existing syngas conversion plants without any significant modification (Arakawa, 1998). Feedstock CO_2 is inexpensive and abundant. Existing and proposed plants for carbon sequestration and storage (CSS) are candidate sources of CO_2. Other resources are flue gas from coal-fired and natural gas-fired electric power plants, gaseous streams in several industrial processes (such as ammonia and hydrogen manufacturing, coal gasification, WGS units, cement factories, aluminium production and fermentation plants) and CO_2 accompanying natural gas and geothermal energy producing wells. After effective separation from air (e.g., by membrane separation or selective absorption technique), excess atmospheric CO_2 offers another