Chemical Engineering Science 87 (2013) 204–208

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

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

Methanol synthesis beyond chemical equilibrium

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HIGHLIGHTS

- Methanol synthesis was visualized in a view cell.
- *In situ* condensation of methanol was demonstrated during methanol synthesis.
- Conversions higher than the chemical equilibrium were obtained.
- Conversions are accurately predicted with a chemical and phase equilibrium model.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 7 July 2012
Received in revised form
12 September 2012
Accepted 7 October 2012
Available online 16 October 2012

Keywords:
Methanol
High pressure
Catalysis
Chemical reactors
Multiphase reactors
Phase change

ABSTRACT

In commercial methanol production from syngas, the conversion is thermodynamically limited to 0.3–0.7 leading to large recycles of non-converted syngas. This problem can be overcome to a significant extent by *in situ* condensation of methanol during its synthesis which is possible nowadays due to the availability of highly active catalysts allowing for lower reactor temperatures. For the first time, *in situ* methanol condensation at 20 MPa and 473 K was demonstrated visually in a view cell. The condensation of reaction products (mainly methanol and water) drives the equilibrium reactions nearly to completion, as is demonstrated experimentally in a packed bed reactor and supported by thermodynamic calculations. Contrary to conventional methanol synthesis, once-through operation becomes possible avoiding recycling of unconverted syngas, which can be economically beneficial for industrial stakeholders.

1. Introduction

Methanol is the simplest of all alcohols and has a wide application range. The global annual production was approximately 38 million metric tons in 2007 and is expected to grow (Berggren, 2011). Methanol is mainly used for the production of bulk chemicals like formaldehyde, acetic acid, and a wide variety of application products including polymers and paints. In addition, methanol has high potential as a clean and renewable energy carrier (Olah et al., 2006). Methanol is produced from syngas, a mixture of H_2, CO, and minor quantities of CO_2 and CH_4. Methanol synthesis proceeds in gas-solid catalytic reactors where three reactions are important: (i) hydrogenation of CO, (ii) hydrogenation of CO_2, and (iii) the water-gas shift reaction:

$$CO+2H_2 \rightleftarrows CH_3OH \quad (1)$$

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http://dx.doi.org/10.1016/j.ces.2012.10.013

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad (2)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (3)$$

There is an ongoing discussion about the actual reactions proceeding in methanol synthesis (Chinchen et al., 1988). For the sake of completeness all three reactions are shown. All reactions are exothermic and reversible. The conversion of $CO+CO_2$ at chemical equilibrium is a function of the pressure and temperature (see Fig. 1).

The first large-scale methanol synthesis plant was constructed by BASF in the 1920s and had to be operated at high temperatures (573–633 K) to compensate for the low catalyst activity (Mittasch et al., 1923; Skrzypek et al., 1994). In order to obtain reasonable conversions high pressures (15–25 MPa) were needed. With the availability of more active Cu-based catalysts and advanced syngas purification techniques operation at lower P and T became possible. As a result, the so-called low pressure methanol synthesis process (5–10 MPa, 490–570 K) was developed by ICI in the 1960s. The majority of the high pressure units has been converted to the low pressure system since then (Skrzypek et al., 1994; Supp, 1990). Both methanol synthesis processes require large recycle flows of syngas due to the limited conversion per reactor pass (Supp, 1990).

The development of more active catalysts allows for even lower reactor temperatures ($473 > T > 520$ K) while high reaction rates are maintained (Zhang et al., 1997). The combination of high pressures (15–25 MPa) and low temperatures, which are the envisaged conditions for this research study, favors high equilibrium conversions towards methanol.

Several studies have been conducted to circumvent the limitations imposed by thermodynamic equilibria and mainly involve *in situ* methanol removal. Examples are methanol adsorption on fine alumina powder or the use of a solvent such as tetraethylene glycol, *n*-butanol, or *n*-hexane (Kuczynski et al., 1987; Reubroycharoen et al., 2003; Westerterp et al., 1989). An alternative method is based on the *in situ* separation of reaction products by condensing them on the surface of a condenser inside the reactor, close to the catalyst bed (Haut et al., 2004). All methods led to higher syngas conversions, but have main drawbacks such as the introduction of other chemicals, complicated operation, or low space time yields. An attractive concept to move beyond chemical equilibrium is to apply *in situ* condensation of methanol without using adsorbents or additional coolers. Condensation is expected to occur at high pressures and low temperatures. To the authors knowledge, condensation has only been shown indirectly by experimental observations of conversions higher than the equilibrium conversions or calculations based on thermodynamic models, (Castier et al., 1989; Hansen and Joensen, 1991; Sorensen and Perregaard, 2004; Topsoe and Hansen, 1993) though has never been demonstrated visually before.

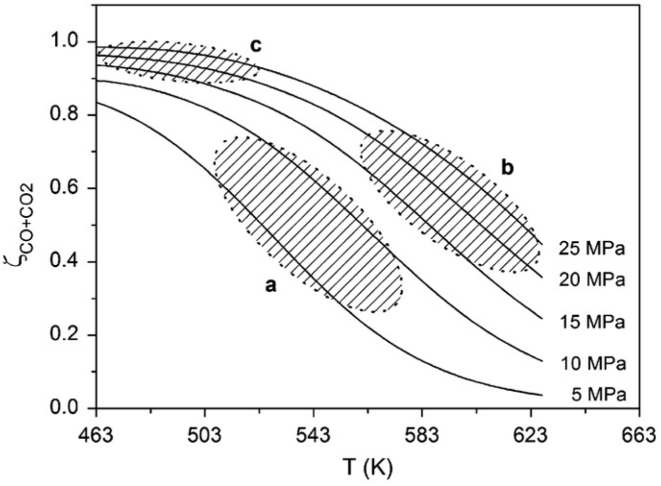

Fig. 1. Equilibria in methanol synthesis. Approximate conditions for: conventional processes (a), BASF's high pressure process (b), this work (c). Syngas: $H_2/CO/CO_2/CH_4 = 0.67/0.24/0.04/0.05$.

Here, we provide the proof of principle for methanol condensation at high pressure (20 MPa) and relatively low temperature (473 K) in a so-called view cell with a transparent window to allow visual observation of the methanol synthesis reactions (Fig. S1, Supplementary data). View cells have been used to investigate phase behavior and precipitation (Adrian et al., 1997; Armellini and Tester, 1991; Briones et al., 1987; Cheong et al., 1986; Japas and Franck, 1985; Jaubert et al., 2001). Its potential for chemical reactions and *in situ* spectroscopy has been recognized, (Caravati et al., 2005; Lefèvre et al., 2011; Moreno et al., 2011; Occhiogrosso and McHugh, 1987; Schneider et al., 2003) though to the authors knowledge, a view cell has not been used so far to perform reactions with heterogeneous catalysts in a stirred cell configuration. In this study the cell contains a typical commercial heterogeneous methanol catalyst ($Cu/ZnO/Al_2O_3$) with high activity.

2. Materials and methods

Experiments were performed in a view cell and a packed bed reactor. Detailed descriptions of both set-ups are included in the Supplementary data. The view cell is a high pressure reactor (32–64 mL) that can be operated at temperatures up to 473 K and pressures up to 60 MPa. The view cell was equipped with either a small basket or a propeller-shaped stirrer. In all view cell experiments cylindrical catalyst pellets were used with a diameter and height of approximately 5 mm. The catalyst used was a commercial $Cu/ZnO/Al_2O_3$ catalyst, but any methanol synthesis catalyst could have been used. The view cell was operated in semi-batch mode at constant pressure (20 MPa) and temperature (473 K).

The packed bed reactor was operated in continuous mode. Pressurized gas was fed via a mass flow controller to a preheater. The gas was heated to the temperature desired, before it was fed to two packed bed reactors ($ID = 10$ mm, $L = 500$ mm) in series. The preheater and the packed bed reactors were heated by an annular heating jacket through which a heating medium was flown. Both packed bed reactors were filled with approximately 50 g of crushed catalyst with particle sizes between 1 and 2 mm. In the first packed bed reactor, a sharp temperature rise occurred and high conversions were already obtained. The second reactor was operated almost isothermally and allows the reaction to proceed till equilibrium. After the packed bed reactor the effluent was cooled in a condenser using tap water. After depressurization a second condenser was used to cool the mixture further. The exit flow was quantified and analyzed and the liquid product was analyzed. The process conditions and syngas compositions used in the experiments are given in Table 1. Syngas 1 resembles a gas which is typically used in methanol synthesis. Syngas 2 has a similar H_2 content but now CO_2 is the main carbon oxide. Such a syngas is interesting as the topic of methanol synthesis from H_2

Table 1
Process conditions of the experiments conducted in the packed bed set-up.

Syngas	T (K)	P (MPa)	H_2 (−)	CO (−)	CO_2 (−)	CH_4 (−)
1	468–543	15–20	0.67–0.68	0.24	0.03–0.04	0.05
2	484–543	20	0.70	0.05	0.20	0.05