



Direct dimethyl ether synthesis from synthesis gas: The influence of methanol dehydration on methanol synthesis reaction



Farbod Dadgar^a, Rune Myrstad^b, Peter Pfeifer^c, Anders Holmen^a, Hilde J. Venvik^{a,*}

^a Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

^b SINTEF Materials and Chemistry, N-7465 Trondheim, Norway

^c Karlsruhe Institute of Technology (KIT), Institute for Micro Process Engineering (IMVT), Hermann-von-Helmholtz-Platz 1, DE-76344 Eggenstein-Leopoldshafen, Germany

ARTICLE INFO

Article history:

Received 2 July 2015

Received in revised form

10 September 2015

Accepted 11 September 2015

Available online 26 October 2015

Keywords:

Methanol synthesis

Methanol dehydration

Direct DME synthesis

Dimethyl ether

Effect of water

ABSTRACT

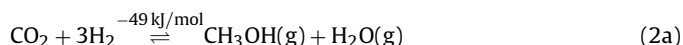
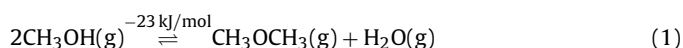
Direct dimethyl ether (DME) synthesis from synthesis gas is studied with regard to potential effects of methanol dehydration on methanol formation and copper-based catalyst performance. For this, the influence of the operating conditions (space velocity, temperature, pressure, time-on-stream and syngas composition) on activity, selectivity and stability of the catalyst was studied and compared for methanol synthesis and direct DME synthesis. The advantage of the direct over the two-step DME synthesis is apparent at conditions where syngas conversion to methanol is thermodynamically limited. However, under the applied operating conditions, results suggest that combining methanol synthesis and dehydration has a negative effect on the methanol formation kinetics. The origin of the observed phenomena is investigated by varying dehydration catalyst and by introducing dehydration products (DME and water) into the methanol synthesis feed. Choice of the solid acid catalyst does not seem to affect methanol formation, and DME is also found to be practically inert over the methanol synthesis catalysts. Water injection, on the other hand, led to a significant decrease in the methanol synthesis rate. Thus, formation of an additional amount of water through methanol dehydration might be an explanation for the lower methanol formation rate in the direct DME synthesis.

© 2015 Published by Elsevier B.V.

1. Introduction

Prior to 1990, dimethyl ether (DME) had a limited commercial application, mainly as a propellant in aerosol spray cans. Over the past few decades, DME usage has grown remarkably by its introduction as an LPG substitute/blendstock for household applications [1]. The pioneering collaborative research efforts by Haldor Topsøe, Amoco and Navistar International Corp. in the 1990s [2,3], drew a lot of attention to DME as a promising alternative fuel for compression ignition engines, due to the high cetane number and low particulate matter emissions, which in turn enable achieving somewhat lower NO_x emissions [4,5]. The conventional DME production route, i.e. methanol dehydration (Eq. (1)), has the drawback of being highly dependent on the price of methanol. In addition, methanol production from synthesis gas (Eq. (2)) is limited by thermodynamic constraints, and to ensure an acceptable overall

conversion a high pressure and a large recycle stream to the reactor is required.



Alternatively, DME can be synthesized directly from synthesis gas using a dual-functional catalyst system that permits both methanol synthesis (over a Cu-based catalyst) and dehydration (over an acidic catalyst) in a single reactor. While syngas conversion to methanol is significantly limited by equilibrium, further conversion of methanol to DME shifts the equilibrium toward more methanol formation and allows higher single-pass conversion. Hence, the direct DME synthesis is thermodynamically and economically more favorable than the two-step process [4,6,7].

In addition to this well-known synergistic effect of methanol synthesis and methanol dehydration, the interactions between the

* Corresponding author.

E-mail address: hilde.j.venvik@ntnu.no (H.J. Venvik).

methanol synthesis and dehydration functions of the direct DME synthesis catalyst have been studied by several research groups. García-Trenco et al. reported detrimental interactions between Cu/ZnO/Al₂O₃ and HZSM-5 in the hybrid catalysts prepared by slurry or grinding methods, leading to a dramatic loss of the available Brønsted acid sites through partial exchange of zeolite protons by Cu²⁺ and Zn²⁺, and blockage of the zeolite micropores by metallic catalyst particles [8]. The same group also found a correlation between the amount of extra framework aluminum (EFAL) species on the external surface of the zeolite and the deactivation of the Cu-based methanol synthesis catalyst during the direct DME synthesis over the hybrid catalyst prepared by grinding [9,10]. They hypothesized that EFAL species may migrate onto the Cu-based catalyst through a water assisted surface diffusion mechanism and modify the interaction between ZnO_x and Cu, causing progressive deactivation of the active copper sites [9]. Ordonsky et al. reported that, in a hybrid catalyst prepared by kneading, the hydroxyl groups on the zeolite outer surface assist copper sintering and migration into the zeolite pores, followed by Cu ion exchange with the zeolite protons leading to deactivation of both the metallic and the acid functions of the catalyst [11]. Peng et al. attributed the catalyst deactivation during slurry-phase direct DME synthesis to a detrimental interaction between the methanol synthesis catalyst and γ -alumina and hypothesized the migration of Cu- and Zn-containing species onto the acid catalyst as the likely mechanism [12]. Such adverse interactions between the metallic and the acid functions of the hybrid catalysts require an intimate solid-state contact between the two components, and hence, are highly dependent on the preparation method of the hybrid [8,9,12,13]. There have been several efforts to minimize these detrimental interactions in the hybrid catalysts with a high degree of inter-dispersion between their two components [11,14].

Another aspect of the interactions between the methanol synthesis and the methanol dehydration during the direct DME synthesis is the possible effect of each step's (by)products on the other step. For one thing, partial pressure of water might be different during the direct DME synthesis compared to its pressure during independent methanol synthesis and independent methanol dehydration under comparable operating conditions. Water introduces diverse effects on both functions of the hybrid catalyst. For instance, high content of water caused by hydrogenation of a CO₂-rich syngas over the metallic component of the hybrid catalyst enhances the deactivation of the Lewis sites of the acid component through strong water adsorption [15]. On the other hand, extra amount of water formed through methanol dehydration over the acid component of the hybrid, enhances the deactivation of the metallic component by assisting morphological changes and hydrothermal leaching of Zn and Al [11,16]. At the same time, water is known to attenuate coke formation and deposition over both functions of the hybrid catalysts [16,17]. Furthermore, formation of hydrocarbons in parallel with methanol synthesis [18,19] or methanol dehydration [20] can eventually lead to carbon compounds deposition and deactivation of both functions of the hybrid catalyst.

Combining methanol synthesis and dehydration in a single step may also pose some effect on the kinetics of the reactions. Such interactions are less discussed in the literature, although limited learnings exist from the literature concerning each of the two steps. Most experimental work regarding the direct DME synthesis has been performed under conditions, at which the independent methanol formation in absence of dehydration would be thermodynamically limited and/or the methanol dehydration influences the overall reaction rate. Hence, the assessment of any potential effects from methanol dehydration on methanol synthesis kinetics is not straightforward. The objective of this work is to provide a better understanding of the effects that combining methanol

synthesis and methanol dehydration in a single reactor can have on the performance of the methanol synthesis catalyst. In order to do this, the influence of operating conditions (space velocity, temperature, pressure, time on stream and syngas composition) on activity, selectivity and stability of the methanol synthesis catalyst was compared for the direct DME synthesis and the methanol synthesis alone under comparable conditions, at which, methanol formation is controlling the overall kinetics and the interference of thermodynamics on the syngas conversion is minimized.

2. Materials and methods

Methanol synthesis was conducted over either a commercial Cu/ZnO-based or a homemade Cu/ZnO/Al₂O₃ catalyst, referred to as CZA for simplicity. The homemade CZA catalyst was prepared by co-precipitation of an aqueous solution of the metal nitrate salts, i.e. Cu(NO₃)₂, Zn(NO₃)₂ and Al(NO₃)₃, with sodium carbonate in a sodium acetate solution at 50 °C and pH 7.0. Precipitates were then filtered, washed thoroughly with deionized water, dried overnight and calcined at 400 °C for 2 h [21]. The resulting homemade catalyst has Cu/Zn/Al molar ratio of 22/57/21 as determined by ICP. Prior to syngas introduction, the catalyst was reduced in situ in a diluted H₂ flow (3% H₂ in N₂) over a 9 h-long stepwise temperature increase, followed by an 8 h treatment at 250 °C. Three different solid acid catalysts were used for methanol dehydration to DME; γ -alumina from Sasol Germany (PURALOX 5/200), ZSM-5 with SiO₂/Al₂O₃ molar ratio of 80 from Zeolyst International (CBV 8014) and NaHZSM-5 prepared from the commercial zeolite. The zeolite was received in ammonium form and calcined in air at 600 °C to produce HZSM-5. An aliquot of the HZSM-5 was treated with a suitable amount of NaNO₃ solution at 75 °C and calcined in air at 600 °C to produce NaHZSM-5. Elemental analysis with ICP-MS confirmed a successful sodium exchange (Na/Al = 12 mol%) and NH₃-TPD showed 10% reduction in the zeolite acidity upon ion-exchange. Hybrid catalysts for the direct DME synthesis from syngas were made by physically mixing the pre-pelletized metallic and acidic catalysts with mass ratio of 8:1 (ZSM-5 as acid function) or 1:4 (γ -alumina as acid function). The catalysts were packed into the reactor as powders in the particle size range 80–125 μ m.

Experiments were conducted in a stainless steel micro packed bed reactor-heat exchanger, fabricated at the Institute of Micro Process Engineering (IMVT), Karlsruhe Institute of Technology. The reactor consists of a 6 cm long reaction slit with rectangular cross section of 8.8 mm \times 1.5 mm, sandwiched between cross flow channels for circulation of a heat transfer oil. Such reactors have been studied earlier under similar operating conditions for the methanol [21–23] and the direct DME [24–26] syntheses, and established as practically isothermal, isobaric, free from mass transfer limitations, and with a narrow residence time distribution.

Premixed synthesis gas with H₂ to CO molar ratio of either 1 (Syngas-1) or 2 (Syngas-2) was used as feed. Composition of both gas mixtures is given in Table 1. Feed flow rates and reactor pressure were controlled using digital mass flow controllers and a digital back pressure controller (Bronkhorst). Introduction of water to the reaction environment was done by evaporating the pressurized deionized water into the feed stream using a Controlled Evaporator Mixer (Bronkhorst). The reaction temperature was monitored by measuring the reactor skin temperature using thermocouples inserted into the holes in the reactor housing, which provide a

Table 1
Composition (mol%) of the applied premixed synthesis gases.

	H ₂	CO	CO ₂	CH ₄	N ₂
Syngas-1	42	42	5	6	5
Syngas-2	56	28	5	6	5

Download English Version:

<https://daneshyari.com/en/article/53259>

Download Persian Version:

<https://daneshyari.com/article/53259>

[Daneshyari.com](https://daneshyari.com)