

DME synthesis at low temperature

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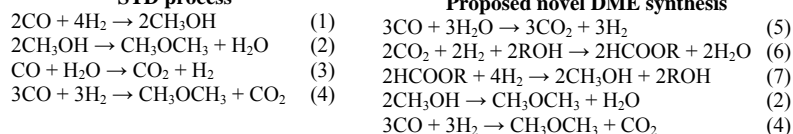
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Introduction

Dimethyl ether is considered as LPG or diesel substitute due to its ease to be liquefied, high cetane number, low emission, and no particulate material [1]. DME is currently produced from syngas through a two-step process, methanol synthesis and methanol dehydration [2] in small quantities and high cost. Therefore, a single-step process, STD (syngas to DME) process has been suggested. This process directly produces DME from syngas by using a hybrid catalyst [3-5]. The single-step process is composed of three reactions.

STD process



Proposed novel DME synthesis

However, DME synthesis (4) is a highly exothermic reaction and generally operated at high temperature and pressure (523-553 K and 3-10 MPa) [6]. At high temperature, the formation of coke on the surface of the catalyst and the metallic sintering deactivate the catalyst severely [5]. In term of economic point of views [4], however, deactivation and syngas recycle can be avoided by operating at low temperature with high one-pass conversion. If methanol synthesis catalyst, which is normally active at high temperature, is still active at low temperature, DME synthesis at low temperature is possible.

Recently, methanol synthesis at low temperature has been successfully reported by the present authors, via a new catalytic route by using Cu-based catalyst and alcohol at 443 K and 5 MPa [7]. This process consists of three reactions: water-gas shift reaction (5); esterification (6); and hydrogenolysis (7). Based on this research, if a suitable acid catalyst is added to dehydrate methanol to DME (2), DME synthesis (4) should be possible at 443 K (low temperature). Herein, a novel DME synthesis at low temperature using alcohol as a catalytic solvent to change the reaction pathway is proposed.

Materials and Methods

The Cu/ZnO catalyst with Cu/Zn molar ratio of 1 was prepared by the co-precipitation. The hybrid catalysts were prepared by physically mixing of the Cu/ZnO catalyst and the acid catalyst (weight ratio of 2:1). The obtained mixture was reduced at 473 K for 13 h by flowing 5% H₂ in N₂ and passivated by 2% O₂ in Ar. The reaction was carried out in a continuous flow-type slurry reactor. The feed gas composition was CO/H₂/Ar = 48/48/4. The product gases were analyzed by GCs equipped with Unibead C (TCD) and Porapak-Q (FID).

Results and Discussion

Table 1 shows that the selectivity of DME was high, indicating that the acidity of HZSM-5 was strong enough to efficiently convert methanol to DME at 443 K. Thus, the low catalytic activity attributed to a low methanol synthesis rate, implying that the overall reaction solely depended on methanol synthesis. In STD process, the reaction route of methanol synthesis was the same as a conventional process in which hydrogenation could not proceed at low temperature. However, an activity of STD process was slightly observed, described by the synergistic effect which one of the products from each reaction is a reactant for the next reaction resulting in a strong driving force for the overall reaction, leading to some activity of STD process. It can be concluded that methanol synthesis is the key to DME synthesis at low temperature.

Table 1. Surface composition via ESCA

Solvent	CO conv. (C-mol%)	Selectivity (C-mol%)			
		DME	MeOH	CH ₄	CO ₂
Paraffin	1	67	0	0	33
Methanol	29	69	0	0	31

Significance

DME can be directly synthesized from syngas at a low temperature (443 K) and 4 MPa via the novel synthesis route.

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