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EVALUATION OF ZEOLITE SUPPORTED CATALYST PERFORMANCE IN DIRECT CONVERSION OF SYNGAS TO DME

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ABSTRACT

The key factor that has important effect on catalyst activity of syngas to DME (STD) reaction is selection of a suitable solid acid catalyst for methanol dehydration. In this regard, zeolites and γ-Al_2O_3 are more applicable catalysts which are evaluated in this review paper. Results from literature, show that generally the activity of zeolites is lower than alumina and to more improvment the activity of zeolites, they are modified by some methods such as subsequent dealumination and introducing a metal compounds into the zeolite structure. According to litreture the best result obtained from addition of Fe, Zr and Mg to HZSM-5, HY and ferrierite zeolite structure. Results showed when acidity of zeolite is high, optimal content of zeolite will be decreased in catalyst. Furthermore, adding of γ-Al_2O_3 to HZSM-5 increased stability of STD catalysts.

INTRODUCTION

Dimethyl ether (DME) is a key intermediate component for the production of many important chemicals such as light olefins, gasoline, LPG, aromatics, dimethoxymethane, hydrogen and so on [1-5]. Since DME has much lower NOx emission, less carbon particulates, no smoke production and less different between its thermal efficiencies and traditional diesel fuel [6], it has a great potential as a clean alternative fuel for diesel engines [7-8]. Because of environmental problems and shortage of crude oil sources, it was predicted that production of DME with lower cost was important in 21st century in the field of chemical engineering. For many years until 1975, DME produced as a byproduct in methanol synthesis procedure so that 3-5wt% of products was DME and separated by distillation from methanol. In 1980 with reformation of methanol synthesis procedure by Lurgi and ICI Co., synthesis of methanol in low pressure became possible and old units completely replaced with these units. But DME production in this unit was low. Therefore, scientists focused to produce DME via catalytic process. In 30 last years, many researches have been carried out by some of companies such as Haldor Topsoe, A/S, Air Product, NKK, corporation, etc. In this paper, catalysts of DME synthesis and effective parameters on their performance are evaluated.

TECHNO-ECONOMIC CONSIDERATION OF DIRECT SYNGAS TO DME: The syngas to DME (STD) reaction is combination of three reaction [13]:

Methanol synthesis	$CO + 2H_2 = CH_3OH$	(1)
Methanol dehydration	$2CH_3OH = CH_3OCH_3 + H_2O$	(2)
Water gas shift (WGS)	$CO + H_2O = CO_2 + H_2$	(3)

DME can be produced in two methods. In first method, the methanol is synthesized in one reactor (reaction 1) then it is converted to DME in the second reactor (reaction 2). Because in this method DME is produced in two separated reactors, it called as indirect method. In other method, syngas is converted to DME in one reactor (whole of 3 reactions are carried out simultaneously). This method called as direct method (STD). In both methods, the water is shifted by the WGS reaction (3) to form carbon dioxide and hydrogen, which is a reactant for reaction (1).

One of advantages of indirect method is saving in time and cost because of known methanol synthesis catalysts and procedure but high cost of methanol as feed and large process lead to increase of DME production cost. On the other hand, as advantages of direct method can be assigned to increasing in syngas conversion to 2 times per one pass of reactor, smaller process in comparison to indirect method and low cost of natural gas in comparison to

methanol as feed. However, because of exothermic nature of STD reaction, this method needs to have complicated controlling system. According to the economic evaluation, the production cost of DME by the STD process is only about 2/3 of the indirect process. This is why the STD process was once developed rapidly along with the development of synthesis gas to gasoline processes [9].

The hybrid catalysts used in STD process are composed of a methanol synthesis catalyst (such as Cu/Zn, Zn/Al, Zn/Cr, Cu/Zn/Al, Cu/Zn/Cr, Cu/Zn/Co, etc.) and a methanol dehydration catalyst (such as silica-alumina [3], TiO_2–ZrO_2 [4] and zeolites like HZSM-5 [1, 5-23], HY, [1] and SAPOs) which are made by physically mixing, impregnation or coprecipitation.

Potential Characteristics of Zeolite Supported Catalysts in DME Process: For methanol dehydration, zeolites and γ-Al_2O_3 are more applicable [4]. It is widely known that active alumina showed high catalytic performance for alcohol dehydration in the point of view of selectivity and life [8]. γ-Al_2O_3 has low price, easy availability and high stability. However, the activity of γ-Al_2O_3 for methanol dehydration in optimum reaction temperature of methanol synthesis is low and the direct synthesis of DME via CO hydrogenation on active alumina supported catalysts must be carried out at higher temperature (270°C). While, increasing in reaction temperature is thermodynamically unfavorable and increases probability of sintering of Cu-sites of methanol synthesis catalysts at high temperatures.

In the literature, for utilization of syngas derived from biomass source, various zeolites are tested whereas Cu–ZnO–Al_2O_3 (CZA) is chosen as CO hydrogenation function. Catalytic activity of different type of zeolite is compared in Figure 1. As shown in this figure, CZA-ferrierite exhibits the highest activity. These results can be affected from better reducibility of the copper species on the surface, its specific topology and proper acidic property that provides higher selectivity towards DME [10].

Results from literature have shown that the activity of zeolites is higher than γ-Al_2O_3 and the former is more applicable in STD process. To improve the activity of zeolites, some strategies are used. Figure shows activity of various zeolitie based catalysts that used in STD process. The best result obtained from addition of Fe, Zr and Mg to HZSM-5, HY and ferrierite zeolite structure.

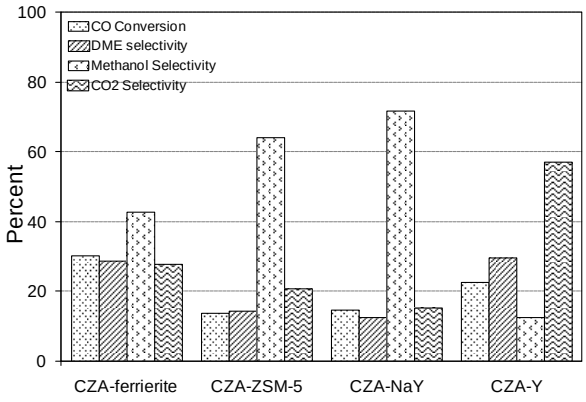

Figure 1
Activity comparison of zeolites in STD reaction [10].

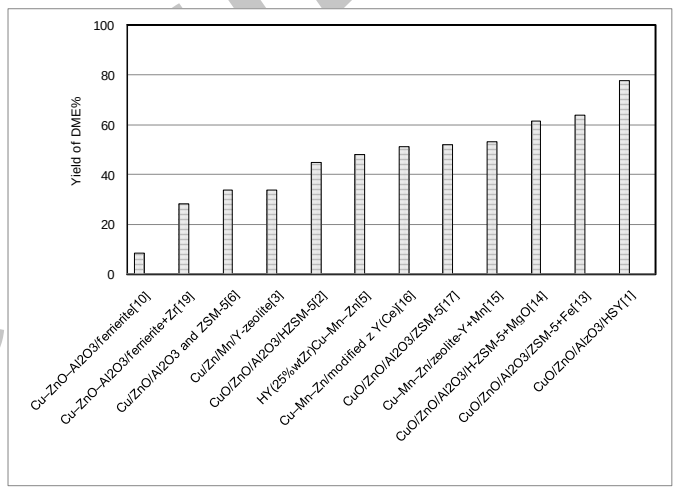

Figure 2
Effect of zeolite content on activity of STD catalysts [10].

Modifications of Acidity of Zeolite Supported Catalysts: The STD catalytic performance heavily depends on strong acidity of zeolites. The relationship between acidic properties and the catalytic performance of solid acid catalysts for methanol dehydration has been studied by many researchers. Most of them have claimed that weak or intermediate strength acid sites are responsible for the selective formation of DME and the strong acid sites may convert the originally formed DME to hydrocarbons [4] and decrease the DME selectivity. In contrast, Kim et al. [5] reported recently that the strong acid sites of HZSM-5 zeolites are responsible for the formation of DME, whereas the relatively weak acid sites appearing below 450 °C in the NH_3-TPD spectra are not important for dehydration of

methanol to DME. With respect to the nature of acid sites, Murzin and co-workers [11] proposed that the Lewis acid sites are active only for methanol dehydration to form DME, whereas strong Brønsted acid sites are required for the transformation of alcohol into hydrocarbons.

Strong acidic sites of HZSM-5 zeolites promote the generation of secondary products like hydrocarbons resulting in low selectivity for DME. Acidity of zeolite directly related to Si/Al ratio of zeolite. With increasing this ratio, acidity decreased. Also the difference of acid strength will change the optimal ratio of the two components. Figure 1 shows that with increasing of Si/Al ratio, DME yield decreased obviously [7].

Another method to improve the activity of STD catalyst is modification of HZSM-5. Acid sites in zeolites are closely related to the tetrahedral aluminium ions in the framework of the zeolite. One method to decrease the content of aluminium in zeolite structures is subsequent dealumination. Another way to reduce acidity is to introduce a metal compound into the zeolite structure. It is well illustrated in the literature that when zeolites was modified with Na, Fe, Mg, Mn, Ce, Zr and so on, the stronger acid sites were eliminated but the weaker acid sites increased [13,14,15, 16].

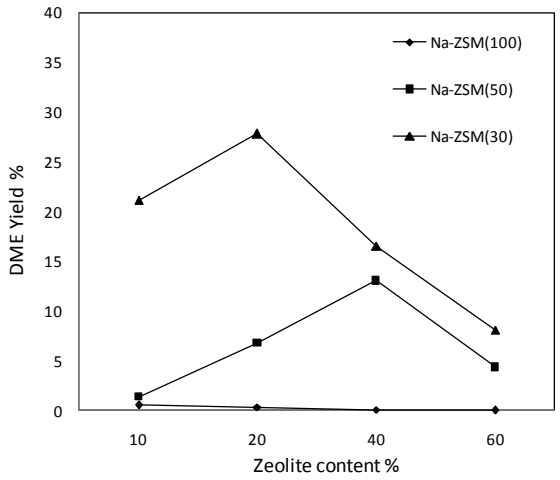

Figure 1
Effect of Si/Al ratio on optimum zeolite content in STD catalysts [6].

Improvement of Catalyst Stability: Operating temperature range is an important requirement for the commercial catalysts in the process of DME production. Because the dehydration of methanol is an exothermic catalytic reaction, the auto acceleration of the side reaction by the reaction heat would often result in temperature runaway and consequently be an obstacle in the using of ZSM-5 catalysts for the commercial dehydration process. Kim et al. [12] showed that modified zeolites by γ-Al_2O_3 show good activity because not only decrease acidity of zeolite but also increase mechanical and thermal stability of catalyst. When the content of γ-alumina increases, the operating temperature range is shifted to a higher temperature range.

CONCLUSIONS

Results from literature shows that in STD process, the activity of alumina is lower than zeolites. To more improvment the activity of zeolites, they are modified by some methods such as subsequent dealumination and introducing a metal compound into the zeolite structure. The best result obtained from addition of Fe, Zr and Mg to HZSM-5, HY and ferrierite zeolite structure. When acidity of zeolite is high, optimal content of zeolite will be decreased in catalyst. It seems using other synthesis methods such as ultrasound or low temperature combustion will produce better structure and higher catalytic activity for zeolites. Furthermore, it is suggested to utilize natural zeolites in STD process because of their low cost.

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