Superior Dehydration of CH_3OH over Double Layer Bed of Solid Acid Catalysts —A Novel Approach for Dimethyl Ether (DME) Synthesis

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A novel catalyst bed packed with two layers of γ-Al_2O_3 and Na-H-ZSM-5 showed an outstanding CH_3OH dehydration activity, total selectivity to DME and longer stability during the reaction time. The TPD of NH_3 confirmed that appropriate amounts of Na-impregnation on H-ZSM-5 drastically reduced the strong acid-sites resulting in 100% selectivity to DME.

Air pollution is a serious environmental concern in all over the world. A large portion of the transport vehicles use diesel fuel. Unfortunately, it emits a significant amount of solid pollutants like unburnt hydrocarbons, NO_x and carbon particulates. With stringent environmental regulations, a clean alternate fuel has become the global necessity. Dimethyl ether (DME) has received a world-wide attention since it has a great potential as a clean alternative fuel for diesel engines because of its thermal efficiencies equivalent to traditional diesel fuel, lower NO_x emission, lesser carbon particulates, near-zero smoke and less engine noise.[1] In addition to its usage as fuel, DME is also useful intermediate for the preparation of many important value-added chemicals such as lower olefins, methyl acetate and dimethyl sulphate.[2,3] In view of this growing demand, there is a need to produce a larger amount of DME in the future.

Commercially, DME is produced by the catalytic dehydration of methanol at around 290 °C and 10 atm over solid acid catalysts such as γ-Al_2O_3.[4–6] In our previous study on the title reaction using γ-Al_2O_3 and H-ZSM-5 independently, we have noticed that γ-Al_2O_3 was found to be active and stable only in the absence of water; while the H-ZSM-5 was highly active in the initial stage of the reaction but slowly deactivated with reaction time due to the formation of lower hydrocarbons.[4–6] However, the remarkable observation was the longer stability of H-ZSM-5 in the presence of water for a period of 100 h.[4] It was also found that modification of H-ZSM-5 with suitable metal cations to remove strong acid sites improved further the dehydration activity as well as the selectivity to DME by preventing the formation of hydrocarbons. Recently, we have reported that when crude methanol containing water was used as a starting material, the formation of hydrocarbons on the hydrophobic surface can be avoided.[4] However, when anhydrous or pure methanol was used as a raw material, the catalyst deactivation was severe with coke formation.[4]

It is known that in the catalytic dehydration of methanol, a significant amount of water is present in the product stream.[5,7–10] Since water adsorbs more strongly on the surface as compared to methanol, the blocking of active sites by water decreases the dehydration activity of methanol more drastically and hence the DME formation. At high water coverage, the heat of adsorption of water on γ-Al_2O_3 is approximately 16 kcal/mol which is consistent with the increase in the activation energy for DME synthesis.[10] Also, the presence of water has the tendency to shift the reaction equilibrium backward. This suggests that the presence of large amount of water will retard the dehydration activity of methanol to DME formation. As a result, hydrophilic γ-Al_2O_3 catalyst located in the bottom bed is not so effective in methanol dehydration. Therefore, it is expected that the efficiency of the catalyst bed could be improved by substituting hydrophobic solid acid catalysts for hydrophilic γ-Al_2O_3 catalyst in the bottom bed of the catalysts.

In this paper, based on our previous studies, a strategy was adopted to design a double layer catalyst bed, having the characteristics resulting from two separate materials viz., γ-Al_2O_3 and Na-H-ZSM-5, and use them as one entity for the dehydration of methanol to DME reaction. According to this scheme, when the reactant methanol contacts the upper layer (γ-Al_2O_3) first, the down-stream products viz., DME, water and the unreacted methanol, would be allowed to contact the bottom layer, Na-H-ZSM-5. By this procedure, the deactivation of Na-H-ZSM-5 can be retarded owing to the presence of water produced over γ-Al_2O_3. In this communication, a double layer bed (γ-Al_2O_3 + Na-H-ZSM-5) showing a remarkable catalytic performance in terms of superior methanol dehydration activity, total selectivity to DME and longer catalyst life is reported. It is the first report of this kind studied on the title reaction at lower temperatures.

Commercial supports, γ-Al_2O_3 (SASOL, $S_{BET} = 220\,m^2/g$) and H-ZSM-5 (ZEOBUILDER, $SiO_2/Al_2O_3 = 40$, $S_{BET} = 403\,m^2/g$) were employed in this study. The Na-modified H-ZSM-5 catalysts were prepared by the conventional impregnation method using an aqueous $NaNO_3$ solution. All the samples were calcined at 823 K for 4 h in air. Methanol dehydration was carried out in a fixed-bed down-flow reactor at a gauge pressure of 10 atm. The double layer bed was arranged in such a manner that 20 vol % of Na_x-H-ZSM-5 was loaded into the bottom bed of the reactor while 80 vol % of γ-Al_2O_3 was loaded into the top bed of the reactor and the total amount of catalyst was 5.0 mL by volume. The symbol (x) in Na_x-H-ZSM-5 refers to the mole percentage of Na^+ based on the mole of H^+ in H-ZSM-5. Before the start of the reaction, the catalyst was activated in the stream of N_2 at 623 K for 1 h under normal atmospheric pressure. Methanol was introduced by a HPLC pump. The products were analyzed by a GC equipped with thermal conductivity and flame ionization detectors.

Figure 1 shows the catalytic dehydration of methanol with reaction time. The γ-Al_2O_3 catalyst showed rather low methanol conversion (<25%). In the industrial process, DME is produced at 290 °C and 10 atm over γ-Al_2O_3 catalyst. In the case of double layer bed (γ-Al_2O_3 + Na_x-H-ZSM-5), the methanol conversions were higher than 80% except γ-Al_2O_3 + Na-ZSM-5.

Because Na-ZSM-5 is totally inactive in methanol dehydration, only γ-Al_2O_3 contributed to the activity in the system composed of γ-Al_2O_3 + Na-ZSM-5. Actually, Na-ZSM-5 did not show any activity in a separate experiment.

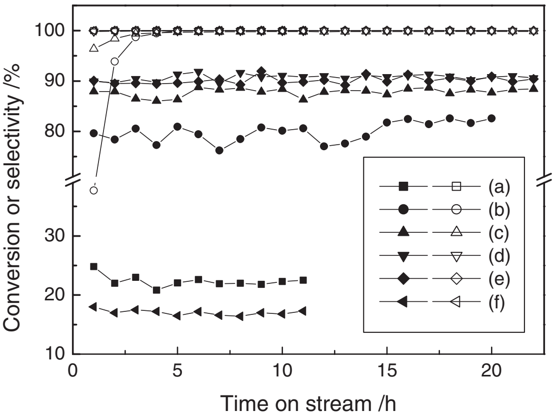

Figure 1. Methanol dehydration to DME over various solid acid catalysts ($T = 250\,°C$, $P = 10\,atm$, LHSV = $4.8\,h^{-1}$, symbol: solid = conversion of MeOH and open = selectivity to DME, γ-Al_2O_3 (a) and double layer bed [γ-Al_2O_3 (top, 2.6 g) + Na_X-H-ZSM-5 (bottom, 0.54 g)] with mol % Na = 10 (b), = 20 (c), = 40 (d), = 80 (e) and = 100 (f)).

Unlike methanol conversion, the DME selectivity strongly depended upon the degree of Na ion impregnated on H-ZSM-5. When 10% Na was impregnated on H-ZSM-5, the initial DME selectivity was less than 40%. This indicates that the hydrocarbons were formed during the course of the reaction. After 3 h, the selectivity towards DME increased to 99%. This is due to the fact that the carbon, formed in the initial stage, eliminated the strong acid-sites responsible for hydrocarbon formation. It is also noticed that as the concentration of Na ions on H-ZSM-5 increased, there was a selectivity of 100% for DME. The acid-sites on H-ZSM-5 are known to be so strong that catalyst deactivation is inevitable during the reaction.[11] The impregnation of the metal ions into H-ZSM-5 catalyst eliminates the strong acid-sites and thereby enhances the resistance towards carbon formation.

Compared with double layer bed composed of γ-Al_2O_3 and Na_{60}-H-ZSM-5, mixed bed having the same composition exhibited lower DME yield at low temperatures (Table 1). In addition, inversely located catalytic system, namely, top bed of Na_{60}-H-ZSM-5 and bottom bed of γ-Al_2O_3, showed much lower DME selectivity (= 40% at 290 °C and 10 atm) resulting from severe hydrocarbon formation in the initial stage. This strongly indicates that the location of the hydrophilic and hydrophobic catalyst is very significant.

Table 1. Comparison of DME yields over double layer bed, mixed bed ($P = 10\,atm$, LHSV = $4.8\,h^{-1}$, catalyst = 2.6 g of γ-Al_2O_3 and 0.54 g of Na_{60}-H-ZSM-5) and γ-Al_2O_3.

Temperature /°C	DME Yield/%		
	Double Layer	Mixed	γ-Al_2O_3
250	86.8	73.2	20.7
260	88.0	81.5	35.6
270	86.3	84.2	61.2
280	86.3	84.9	64.5
290	86.7	83.9	76.9

According to NH_3-TPD results on Na_x-H-ZSM-5 (data shown as a supplementary data), it is explicit that the surface density of the strong acid-sites, in the region of 330 to 500 °C, decreased with increase in sodium level on H-ZSM-5. In addition, it is noticed that there is a small shift in the position of T_{max} of the third peak towards the region (220 to 330 °C) of medium acid-sites, whose density, though not quantified, has increased. These observations clearly demonstrate that a novel catalyst bed packed with two layers of hydrophilic γ-Al_2O_3 and a hydrophobic Na-H-ZSM-5 provides highly active and selective way in the methanol dehydration reaction to DME. The catalyst, having 40–80% Na-content, in Na-H-ZSM-5 showed an optimum performance in terms of activity and selectivity ($C_{MeOH} = 89\%$, $S_{DME} = 100\%$) with an exceptional stability for 400 h under the same reaction conditions.

In conclusion, the double layer catalyst bed, γ-Al_2O_3 + Na-H-ZSM-5, demonstrates a higher catalytic activity as well as 100% selectivity in the conversion of methanol to DME at low temperatures. This is possibly ascribed to the synergy effect shown between the hydrophilicity of γ-Al_2O_3 and the hydrophobicity of Na-H-ZSM-5. The reduction in the surface density of strong acid-sites by Na-modification of H-ZSM-5 further increases selectivity to DME and makes the catalyst more resistant towards carbon and/or hydrocarbon formation. Finally, it is our anticipation that the double layer bed of this combination would be a suitable candidate for the industrial production of DME from methanol at low temperatures in the near future.

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