

DIMETHYL ETHER (DME) SYNTHESIS

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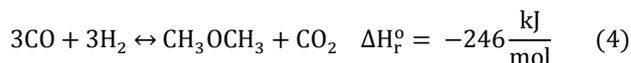
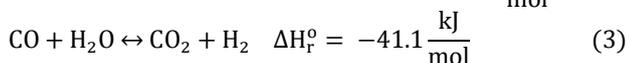
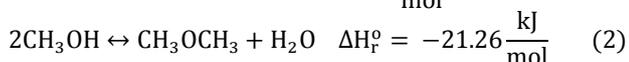
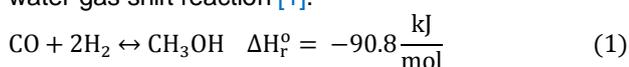
ABSTRACT

Understanding the stability of the catalyst is thus critical when designing new catalysts/processes able to achieve clean fuel for practical applications. An example of the stability study is CuO-ZnO-Al₂O₃/HZSM-5 bifunctional catalyst of one step dimethyl ether (DME) synthesis. This catalyst showed high stability over a period of 212 hr but it lost around 16.2 % of its initial activity. After TPO investigation the catalyst deactivation could be explained by 3 types of coke deposited: on the metallic sites; on the interface between the metallic sites and the support near the metal-support; and on the support.

Different solid acid catalysts (NH₄ZSM-5, HZSM-5 or γ -Al₂O₃) as a dehydration function were physically mixed with CZA for direct DME synthesis from syngas. It was found that the CZA/ HZSM-5 bifunctional catalyst with 0.25 acid fraction showed high stability over a period of 212 hr.

1. INTRODUCTION

Dimethyl ether (DME) is the simplest ether with chemical formula of CH₃OCH₃. It is a colourless gas at ambient conditions. Its boiling point at atmospheric pressure is -25.1 °C but can be easily liquefied at a low pressure of approximately 6 atmosphere at 303 K. Thus, DME can be handled as a liquid. It can be used as a fuel in diesel engines and works particularly well in such engines due to its high cetane number, which is greater than 55 compared to about 40-55 for diesel fuel. Due to its attractive properties and economic benefits DME has recently gained more industrial attention. Traditionally DME is produced from methanol dehydration. But, recently the Syngas -to- DME (STD) process was developed for DME synthesis over a hybrid catalyst with the two functions, metallic and acid. The STD reaction system allows greater productivity in a single reactor system because of the synergy among the three reactions. The main reactions take place in STD, methanol synthesis, methanol dehydration and water-gas shift reaction [1].



Catalysts for the STD process are usually composed of a methanol synthesis catalyst which usually contains zinc, copper, and aluminum oxides and a solid acid catalyst for methanol dehydration, which the most common solid acids applied in STD process, are γ -Al₂O₃ and HZSM-5. Copper based catalysts are considered to be the standard for methanol synthesis (metal function). Industrially a CuO/ZnO/Al₂O₃ (CZA) catalyst is commonly used as a metallic function for MeOH synthesis reaction. The currently used industrial CZA catalysts are usually operated at 493–553 K. The reaction at lower temperature leads to the low reaction activity, while higher temperature results in the sintering of the catalysts. Thus, an ideal dehydration component must be operated within the temperature range of the CZA catalyst that is if it is used with CZA for the direct synthesis of DME. Therefore it must be highly active and stable in the temperature range from 493 to 553 K [2].

Commercially, γ -Al₂O₃ is used to a large extent for such reactions. Though Al₂O₃ is active, it tends to adsorb water on its surface and thereby loses its activity in the presence of water because of its hydrophilic nature. Also, γ -Al₂O₃ is less active than zeolites such as ZSM-5 due to its weak acidity. Among the solid acids used for the dehydration of methanol to DME, H-ZSM-5 was reported by to be the best dehydration catalyst for DME synthesis from syngas [3]. On the other hand; some researchers reported that hydrocarbons were formed at 270 °C or at higher temperatures when HZSM-5 zeolite was used as a methanol dehydration catalyst. These results are due to the strong acidity and the large amount of acidic sites of H-ZSM-5 that dehydrate methanol to hydrocarbons and then form coke on the surface of H-ZSM-5 [4].

The typical composition of syngas used in MeOH synthesis is H₂:CO ratio of 2:1 with 1-4% CO₂ in which with this percent of CO₂ the methanol production rate and activity was found to be the maximum [5].

The objective of this work was to investigate the activity of the admixed catalyst made of CZA as methanol synthesis catalyst and various solid acids (NH₄ZSM-5(SiO₂/Al₂O₃=80), HZSM-5 (SiO₂/Al₂O₃=80), NH₄ZSM-5(SiO₂/Al₂O₃= 23), γ-Al₂O₃ and 10% MgOZSM-5(SiO₂/Al₂O₃=80)) as the MeOH dehydration function with metal to acid ratio is 2. On the other hand, the effect of acid fraction in the CZA/γ-Al₂O₃ and CZA/HZSM-5(80) admixed catalyst and the stability (aging) of the admixed catalyst during the storage. In addition the long term time on stream stability of the admixed catalyst and the nature of deactivation of the metallic and acidic functions of used admixed catalyst by using TPO.

2. EXPERIMENTAL

2.1 CATALYST PREPARATION

2.1.1 Material

The chemicals used in the present study were all analytical grades and supplied by Aldrich, UK. These were copper nitrate [Cu(NO₃)₂·2.5H₂O], zinc nitrate [Zn(NO₃)₂·6H₂O], aluminum nitrate [Al(NO₃)₃·9H₂O] and sodium carbonate Na₂CO₃,

2.1.2 CuO/ZnO/Al₂O₃ Catalyst

The CuO/ZnO/Al₂O₃ catalyst was prepared by a conventional co-precipitation method with a wt% ratio of CuO:ZnO:Al₂O₃=6:3:1. The mixed solutions of copper, zinc and aluminum nitrate and an aqueous solution of Na₂CO₃ were added drop wise, under continuous mixing at 70 °C. The pH was adjusted to seven during precipitation by controlling the flow rates of two liquids. After precipitation, the precipitate was aged at the same temperature under continuous stirring. The precipitate was then filtered and washed several times with deionized water to remove residual sodium ions and then the solid obtained was dried at 120 °C for 12 h and calcined at 500 °C for 6 h. For simplicity this catalyst is designated and labelled as CZA.

2.1.3 Solid Acid Catalyst

The γ-Al₂O₃ acid function has been prepared by crushing of γ-Al₂O₃ pellets. A commercial NH₄-ZSM-5 and HZSM-5 zeolite with (SiO₂/Al₂O₃=80, 23) were used. For simplicity these catalysts are designated and labelled as NH₄ZSM-5(80), NH₄ZSM-5(23), HZSM-5(80) and HZSM-5(23).

2.1.4 Admixed Catalyst for Direct DME Synthesis

The admixed catalyst was prepared by kneading the mixture of the dry metallic function and the acid function powders in an agate mortar to form homogenous mixture, the resultant powder was pressed to tablets and then crushed and sieved to the particles of 0.25-0.425 mm (in diameter).

2.2 CATALYST ACTIVITY FOR DME SYNTHESIS

The DME synthesis were carried out in an isothermal fixed bed reactor made of stainless steel with an inner

diameter of 6 mm placed in ceramic tube furnace controlled by eurotherm2604 controller. Typically 250 mg of the catalyst was placed in the reactor. After that the catalyst was exposed to the syngas mixture (BOC gases) contained (62% H₂, 31% CO, 4% CO₂ and 3% Ar) [6, 7]. The activity tests were carried out in the following conditions: a temperature range from 200 to 260 °C, a pressure from 20 to 50 bar and a space velocity of syngas mixture of 2640 ml.h⁻¹.g⁻¹.cat. On-line analysis of the reactants and products were measured using Perkin Elmer; Clarus 500 Arnel valved gas chromatograph, equipped with a thermal conductivity detector (TCD) and Auto-Ignite Flame Ionisation Detector (FID). The equipment setup used in this study is represented in Fig. 1.

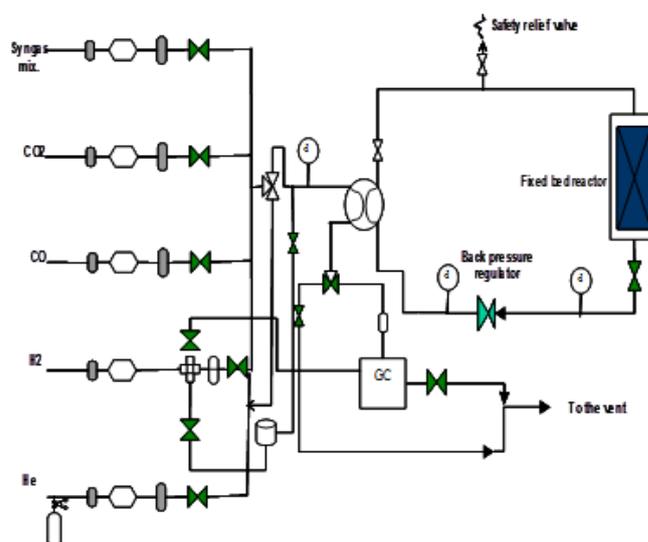


Fig. 1. DME Equipment setup.

2.3 CATALYST CHARACTERIZATION

The acidity of the samples was measured by NH₃-TPD. It was performed using 50 mg of the catalyst after pretreatment at 500 °C for 90 min in a 10% O₂/He or 5% H₂/Ar flow. The sample was saturated with NH₃ for 30 min at 150 °C. After saturation, the sample was purged with He for 45 min to remove physically adsorbed NH₃ on the surface of the catalyst. The temperature of the sample was then raised from 150 to 700 °C using a TCD detector.

The reducibility of the catalysts was investigated using TPR technique. All the TPR experiments were performed on a Micromeritics Autochem 2910 apparatus and the H₂ uptake was monitored by a TCD from -50 to 700 °C under flowing 5% H₂/Ar. Before TPR analysis, all the samples were pretreated at 500 °C under flowing 10% O₂/He, and then the temperature was decreased to -50°C under flowing Ar before starting the TPR experiment.

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to determine the actual amount of metals (Cu, Zn, Al and Au) in the calcined catalyst.

3. RESULTS AND DISCUSSION

3.1 CATALYST ACTIVITY TESTING

3.1.1 CZA catalyst activity

Fig. 2 shows the comparison of theoretical equilibrium conversion and experimental CO conversion for CZA @ 20 bar. It is clear that CZA catalyst is active at high temperatures in which the CO conversion ($X_{CO}=20.5\%$) reached the equilibrium conversion ($X_e=21.3\%$) @ 250 °C and 20 bar but it is far away ($X_{CO}=6.2\%$) from the equilibrium conversion ($X_e=60.8\%$) at 200 °C and 20 bar.

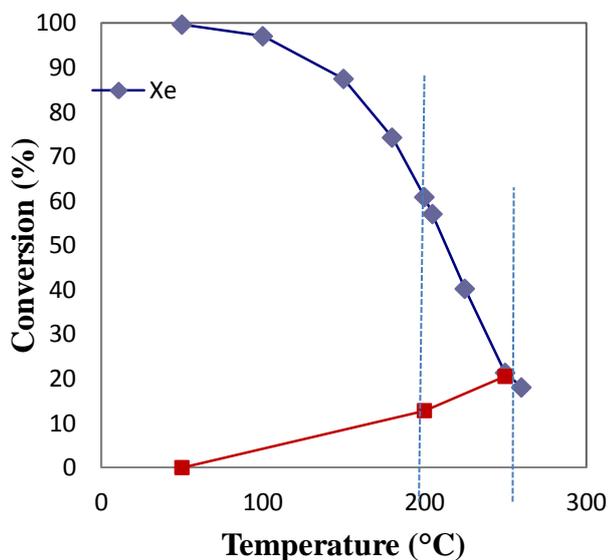


Fig. 2. Comparison of theoretical equilibrium conversion and experimental CO conversion for CZA @ 20 bar

3.1.2 DME Synthesis

Fig. 3 and Fig. 4 show the % of DME and MeOH for different admixed catalysts. All the catalysts in these figures were prepared by physically mixing of the CZA catalyst and solid acid catalyst; the metal to acid ratio is kept 2. As shown in Figure (3) and Table (1) that there is no big differences in DME production rate for the admixed catalysts containing acid function $NH_4ZSM-5(80)$, $HZSM-5(80)$ and $NH_4ZSM-5(23)$, which means that the MeOH dehydration reaction is controlled by the number of more acidic site and not by the strength of the acid function and there is no difference in number of acidic sites between acid function. As a consequence, the overall one step DME synthesis is not controlled by MeOH dehydration reaction and the rate limiting step is the MeOH synthesis reaction. The % of DME produced for the admixed catalyst containing acid function $\gamma-Al_2O_3$ and 10% $MgOZSM-5(80)$ is 5% and 1%, respectively. Such a decrease in the DME production is related to the mild acidity of $\gamma-Al_2O_3$ and weak acidity of 10% $MgOZSM-5(80)$. Therefore, for these acid functions, the overall one step DME synthesis is controlled by MeOH dehydration reaction and the rate limiting step is the MeOH dehydration reaction. As shown in Figure (4) the concentration of methanol increased as the acidity of the acid function decreased which confirms that the rate limiting step of weak acids

is the MeOH dehydration reaction. Mao et al.[8] studied the effect of modification of HZSM-5 zeolite with various contents of MgO (0-10 wt%) and then physically admixed with CZA methanol synthesis catalyst to form the admixed catalysts. They found that the hybrid catalyst containing the MgO with 10 wt% exhibited the lowest selectivity of DME and the highest selectivity of MeOH due to its low acidity, which is in agreement with our results.

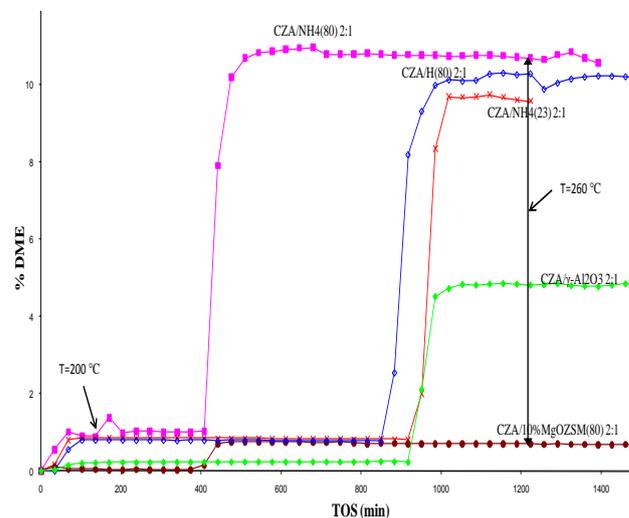


Fig. 3. % DME using different acid function catalysts

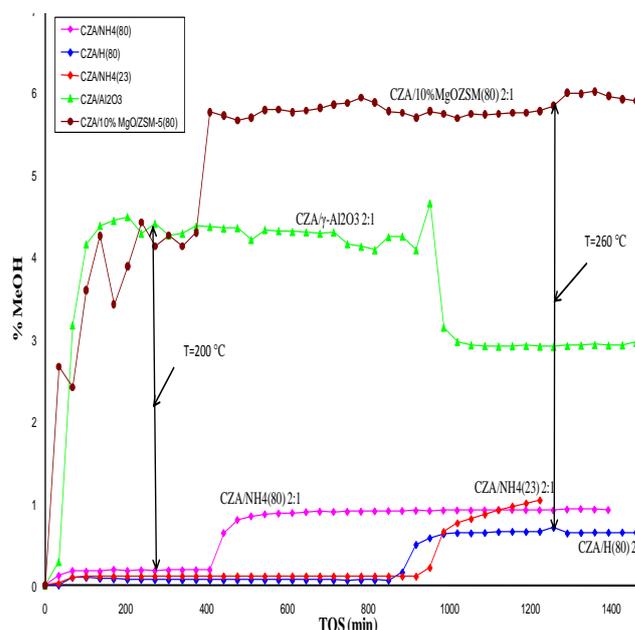


Fig. 4. % MeOH using different acid function catalysts

Table (1) shows the effect of temperature (205 and 260 °C) on the activity for different admixed catalysts. All the catalysts in this table were prepared by physically mixing of the CZA catalyst and solid acid catalyst; the metal to acid ratio is kept 2. From Table (1), it can be seen that ethylene formation started when the temperature increased from 200 to 260 °C, as DME dehydration occurs at high temperature. It can be seen

also that the amount of by products (ethylene and others) for all admixed catalyst mentioned above is negligible therefore the CO conversion (X_{CO}) is calculated assuming there are no byproducts. The synergetic effect of combining the metal and acid function can be seen by comparing the conversion of CO in MeOH synthesis catalyst alone with the admixed catalyst of DME synthesis which increased from 20.6 % to around 63 %.

Table 1. Effect of operating temperature on the catalytic performance of different admixed catalyst for the direct DME synthesis from syngas. @ P=20 bar and metal to acid ratio is 2.

Catalyst	X_{CO} (%)		DME (%)		MeOH (%)		C_2H_4 (%)		CO_2 (%)	
	205 °C	260 °C	205 °C	260 °C	205 °C	260 °C	205 °C	260 °C	205 °C	260 °C
CZA/NH4ZSM-5(80)	6.38	63.43	1	10.8	0.19	0.92	0	0.017	4.05	11.8
CZA/NH4ZSM-5(23)	4.72	59.24	0.84	9.6	0.11	1	0	0.034	3.87	11.2
CZA/HZSM-5(80)	3.97	59.77	0.77	10	0.06	0.62	0	0.025	3.8	11.2
CZA/ γ - Al_2O_3	12.24	37.74	0.24	4.6	4.3	2.9	0	0.011	3.76	7.4
CZA/10% MgOZSM-5(80)	10.18	19.76	0.033	0.64	4.2	5.9	0	0	3.5	4.4
CZA	12.8	20.5	0	0.02	4.3	7.6	0	0		

3.2 CATALYST CHARACTERIZATION

3.2.2 Admixed Catalyst Characterization

3.2.2.1 Temperature Program Reduction (TPR)

Fig. 5 shows the TPR for the admixed catalysts. It is clear that there is only one broad reduction peak appearing in the range of 150–350 °C. In general, a clear single reduction peak, without any shoulder, indicates that the CuO is well dispersed on the support surface [9]. It can be seen that all the catalysts have the same peak intensity during the same period of time.

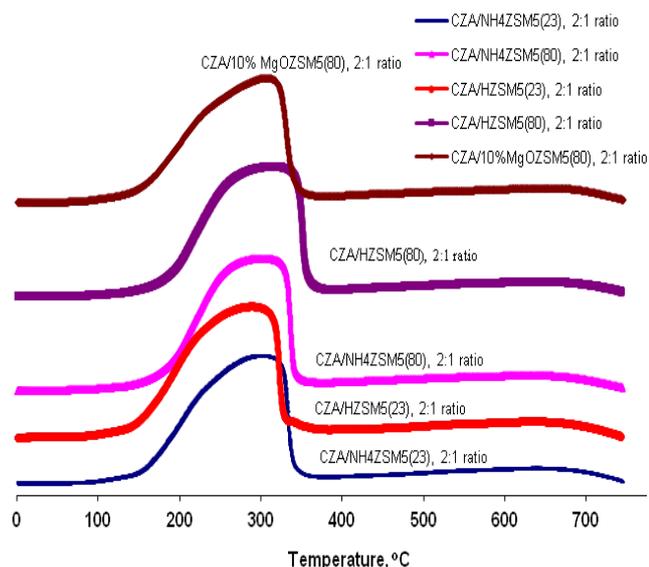


Fig. 5. TPR patterns for the admixed catalyst

3.2.2.2 NH_3 -Temperature Program Desorption (NH_3 -TPD)

Fig. 6 shows the TPD profiles of NH_3 desorption on the surface of the solid acid catalysts in fresh and reduced phase of solid acid catalysts. It is clear that there is no difference between the reduced and unreduced phase for all acid solid catalysts which is in agreement with TPR results. Each profile shows two distinct regions except γ - Al_2O_3 . The peak at 250-350 °C corresponds to the weak acid sites whereas the peak at higher temperature around 450-550 °C was attributed to the strong acid sites [4, 10]. It is clear that the high temperature peak intensity increased as SiO_2/Al_2O_3 decreased, at $SiO_2/Al_2O_3=23$. This was attributed to the increase in extra-framework aluminium content as well as the in the framework [11]. It can be seen also that with the decrease of SiO_2/Al_2O_3 , the desorption temperature of NH_3 from the strong acid sites shifted to higher temperature which strongly proves the existence of aluminum in extra-framework positions which is in agreement with Shirazi et al.[11]. Xu et al.[12] have proved that for low (SiO_2/Al_2O_3) ratio in HZSM-5, the Brønsted (strong) and Lewis (weak) acid sites play role in the MeOH dehydration reaction and as the ratio increased, the solid acid exhibits only strong acid sites since there is no extra-framework aluminum. As shown in the figure the area below the TPD curves, which indicates the total number of acid sites on the surface of catalyst [13], decreases in the order of HZSM-5(23) > HZSM-5(80) > γ - Al_2O_3 .

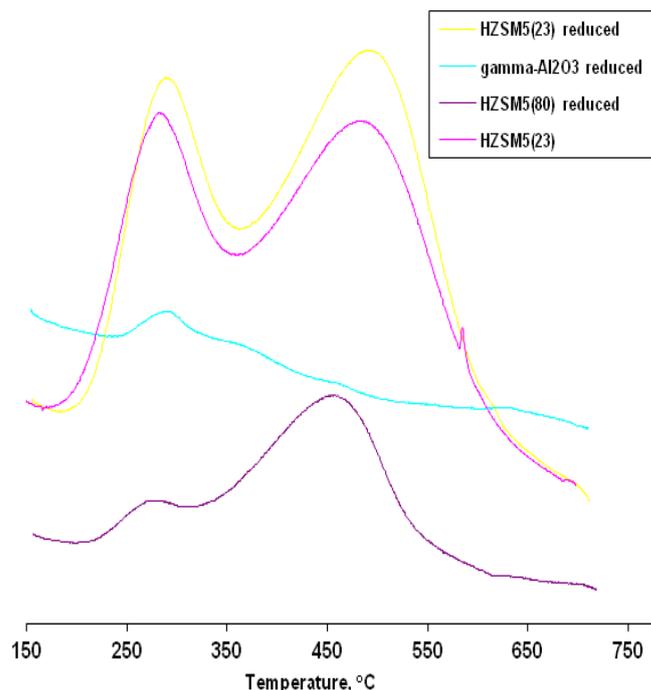


Fig. 6. Comparison of NH_3 -TPD profiles of reduced and unreduced solid acid catalysts

4. CONCLUSION

Different acid solid catalysts were studied as a dehydration component in direct DME synthesis (NH_4 ZSM-5 ($SiO_2/Al_2O_3=23$, 80), HZSM-5 ($SiO_2/Al_2O_3=80$) or γ - Al_2O_3). It was found that the HZSM-5 catalyst has the most stable acid function

during the storage. HZSM-5 catalyst also possessed high activity for the dehydration reaction at relatively low temperature compared with $\gamma\text{-Al}_2\text{O}_3$.

5. REFERENCES

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