Activity and deactivation studies for direct Dimethyl Ether Synthesis using CuO-ZnO-Al$_2$O$_3$ with NH$_4$ZSM-5, HZSM-5 or γ-Al$_2$O$_3$

Jehad Abu-Dahrieh, David Rooney, Alexandre Goguet, Youssef Saih

PII: S1385-8947(12)00902-3
Reference: CEJ 9526

To appear in: Chemical Engineering Journal

Please cite this article as: J. Abu-Dahrieh, D. Rooney, A. Goguet, Y. Saih, Activity and deactivation studies for direct Dimethyl Ether Synthesis using CuO-ZnO-Al$_2$O$_3$ with NH$_4$ZSM-5, HZSM-5 or γ-Al$_2$O$_3$, Chemical Engineering Journal (2012), doi: http://dx.doi.org/10.1016/j.cej.2012.07.011

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Activity and deactivation studies for direct Dimethyl Ether Synthesis using CuO-ZnO-Al$_2$O$_3$ with NH$_4$ZSM-5, HZSM-5 or γ-Al$_2$O$_3$

Jehad Abu-Dahrieh$^a$, David Rooney$^{a*}$, Alexandre Goguet$^a$, Youssef Saih$^a$

$^a$CenTACat, Queen’s University Belfast, Belfast BT9 5AG, Northern Ireland, UK.

* Corresponding author

David Rooney

E-mail: d.rooney@qub.ac.uk

Address: School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, United Kingdom

Fax: +44 2890 97 4687

Tel.: +44 2890 97 4050
Abstract

Herein we investigate the use of CuO-ZnO-Al$_2$O$_3$ (CZA) with different solid acid catalysts (NH$_4$ZSM-5, HZSM-5 or γ-Al$_2$O$_3$) for the production of dimethyl ether from syngas. It was found that of the solid acids, which are necessary for the dehydration function of the admixed system, the CZA/HZSM-5 bifunctional catalyst with a 0.25 acid fraction showed high stability over a continuous period of 212 hr.

As this particular system was observed to lose around 16.2% of its initial activity over this operating period this study further investigates the CZA/HZSM-5 bifunctional catalyst in terms of its deactivation mechanisms. TPO investigations showed that the catalyst deactivation was related to coke deposited on the metallic sites; interface between the metallic sites and the support near the metal-support; and on the support itself.

Keywords: Methanol synthesis, DME synthesis, Methanol dehydration, CuO/ZnO/Al$_2$O$_3$ catalyst, acid catalyst, syngas.
1. Introduction

Dimethyl ether (DME, CH$_3$OCH$_3$) is the simplest of the ethers and although a gas at ambient conditions (normal boiling point of -25.1°C) it can be easily liquefied at low pressures ($\approx$ 6.06 bar at 30°C) and can thus be handled as a liquid in many applications. Recently it has been considered as an alternative fuel for diesel engines particularly given its high cetane number, which is greater than 55, when compared with 40-55 for diesel fuel. Due to this and other attractive properties such as biodegradability and other economic benefits of producing such fuel, DME has recently gained significantly more industrial attention.

Traditionally DME is produced from methanol dehydration. However, recently Syngas -to- DME (STD) processes have been developed for direct DME synthesis over hybrid catalysts containing two functionalities, i.e. metallic for methanol production and acid for methanol dehydration. The STD reaction system allows greater productivity in a single reactor system because of the synergy among the three reactions leading to thermodynamic improvements. Overall the main reactions taking place in the STD process are methanol synthesis Eq. 1, methanol dehydration Eq. 2 and water-gas shift reaction Eq. 3 [1]. When all three steps Eq. 1 to Eq. 3 take place, the equations are combined to form Eq. 4 [2]:

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \leftrightarrow \text{CH}_3\text{OH} \quad \Delta H^\circ = -90.9 \text{ kJ mol}^{-1} \\
2\text{CH}_3\text{OH} & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H^\circ = -21.26 \text{ kJ mol}^{-1} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -41.1 \text{ kJ mol}^{-1} \\
3\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2 \quad \Delta H^\circ = -246 \text{ kJ mol}^{-1}
\end{align*}
\]
Catalysts for the STD process are thus usually composed of a methanol synthesis catalyst and a solid acid catalyst for methanol dehydration, for which the most common solid acids are $\gamma$-Al$_2$O$_3$ and HZSM-5[3-6]. Copper based catalysts are considered to be the standard for methanol synthesis (metal function) with the most common being a CuO/ZnO/Al$_2$O$_3$ (CZA) catalyst used under typical conditions of 220–280 °C and 50 to 100 bar [7]. 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 operate within the temperature range of the CZA catalyst that is if it is to be used for the direct synthesis of DME [8].

Commercially, $\gamma$-Al$_2$O$_3$ is used to a large extent for acid catalysed dehydration reactions[3, 9]. Although Al$_2$O$_3$ is active, it tends to strongly adsorb water and thereby loses activity. Also, $\gamma$-Al$_2$O$_3$ is less active than zeolites such as ZSM-5 due to its relatively weak acidity. Among the solid acids used for the dehydration of methanol to DME, H-ZSM-5 was reported to be the best for DME synthesis from syngas[10]. On the other hand; some researchers reported that hydrocarbons were formed at 270 °C or at higher temperatures with this catalyst. These results are due to the combination of strong acidity and the acidic sites density of H-ZSM-5 that dehydrate methanol to hydrocarbons and can lead to the formation coke on the surface [5].

The preparation method of the bifunctional catalyst system for direct DME synthesis has a significant effect on the performance of the process. Generally, two different methods of combining methanol synthesis function and solid acid function can be summarized as either hybrid (composite) or admixed catalysts. For the former the
methanol synthesis and methanol dehydration catalyst components exist together as a single entity [11]. Such catalysts are generally prepared by coprecipitation or mixing of the freshly precipitated precursors [12-15]. While in the case of the admixed catalyst each function is prepared (synthesized) separately and then the powders of both functions are mechanically blended [16-22]. It is important that the contact between these functions does not cause blockage of active site for the other. Contact between functions depends on the preparation method of the bifunctional catalyst. In some cases the acidity of the bifunctional catalysts presented a lower value than expected due to the partial blockage of acid sites by the methanol synthesis component [23]. Kawabata et al. [24] demonstrated that the performance of a bifunctional catalyst made up of CZA and HZSM-5 zeolite was improved by preparing it by physically mixing both components and then pelletizing. Wang et al. [19] looked at the synergistic effect of physically mixing methanol synthesis and dehydration catalysts. These results showed that the mixing of two functions enhanced the CO conversion through the chemical synergy between methanol synthesis and dehydration reactions.

Since the 1980s, the main focus of most published scientific literature in this area has been on catalyst development. Several groups have studied the acid property of the catalyst for the STD process. Aguayo et al.[14], Xu et al.[4], Jiang et al.[3], Roh et al.[25] and Kim et al.[5] proved that pure γ-alumina exhibited much lower activity than the H-ZSM-5 and ZSM-5 catalysts modified with Na. Joo et al. [26] studied the effect of the treatment of H-ZSM-5 and γ-alumina with formaldehyde and sodium carbonate. They found that the modified catalysts showed enhanced selectivity to DME, minimizing the reforming reaction to carbon dioxide. Tokay et al.[27] studied catalytic performances of different modified alumina based catalysts for methanol
dehydration. Kim et al. [5] studied the effect of $\gamma$-alumina as a binder on the catalytic performance of Na-modified ZSM-5 and reported that a Na-H-ZSM-5 containing 70% of $\gamma$-alumina as a binder was active and stable in the conversion of methanol to DME. Fei et al. [28] studied the synthesis of DME via methanol dehydration over HY zeolite and over Fe-, Co-, Ni-, Cr-, or Zr-modified HY zeolite, and via direct CO hydrogenation over modified HY zeolite-supported Cu–Mn–Zn catalysts. They found that Zr- and Ni-modified HY zeolite exhibited the highest activity and stability for methanol dehydration, while Fe-, Co-, and Cr-modified HY zeolite deactivated quickly due to carbon deposition. They also found that the fraction of dehydration component had an important influence on the performance of the bifunctional catalyst. In this work a Zr–HY supported Cu–Mn–Zn catalyst was more active and stable than Cu–Mn–Zn/HY in the STD process. Mao et al. [29] studied a series of $\gamma$-Al$_2$O$_3$ samples modified with various levels of sulfate (0–15 wt.%) and calcined at different temperatures. These were prepared by an impregnation method and physically admixed with CZA to form hybrid catalysts. They found that the hybrid catalyst containing the SO$_4^{2-}$/γ-Al$_2$O$_3$ with 10 wt.% sulphate and calcined at 550 °C exhibited the highest selectivity and yield for the synthesis of DME.

Other research has focused on the metallic function in the combined catalyst. Fei et al. [30] for example studied the effect of copper content in the Cu–Mn–Zn/zeolite–Y catalyst and reported that an increasing value of Cu is conducive to enhancing its activity for direct synthesis of DME from CO hydrogenation. A catalyst with a Cu/(Cu+ Mn + Zn) ratio up to 0.6 exhibited the best performance. Tan et al. [31] studied the promotional effect of Mn on the activity and the stability of CZA catalyst
for DME synthesis from syngas in the slurry phase. In this work they found that a Mn-modified CZA catalyst has high activity and good stability. Lee et al. [32] studied the effect of preparation method on the catalytic performance of CuO/ZnO based catalysts by varying the conditions of coprecipitation, promoters and nanoparticles. They found that the addition of Ga$_2$O$_3$, MgO and ZrO$_2$ as promoters improved activity and life time. Fei et al.[33] prepared a series of copper-based catalysts supported on zeolite-Y by a coprecipitation impregnation method and found that the selectivity to DME on a Cu-Mn-Zn/zeolite-Y catalyst was ten times that of Cu/zeolite-Y.

Many researchers have studied the effect of preparation method on the bifunctional catalyst. For example Moradi et al.[15] studied the effect of different preparation methods on catalytic properties and physical structure of CZA as a hybrid catalyst and the effect of alumina content at a fixed CuO/ZnO ratio on the performance of the hybrid catalyst STD conversion. They also developed a novel method of preparation namely sol–gel impregnation and found that the optimum weight ratio for CuO: ZnO: Al$_2$O$_3$ catalyst was 2:1:5, respectively. In a subsequent paper Moradi et al.[18] looked at the catalyst activity of physically mixing CZA catalysts with different acid functions (γ-Al$_2$O$_3$, HZSM-5 and H-Mordenite). The results showed that the CZA/HZSM-5 catalyst had the best performance. Lu et al.[34] used CZA/HZSM-5 catalyst prepared by the coprecipitation deposition method and studied the activity at different temperatures. They found that the optimum ratio of the two components was about 5.0 for CZA/HZSM-5 catalyst.
Moradi et al.[35] prepared nine hybrid catalysts and found that physically mixing catalysts showed better performance than the other preparation methods while Ramos et al.[16] showed that the rate limiting step of DME direct synthesis was determined by the acid properties of the dehydrating catalyst, i.e., its acid strength and number of acid sites. On the contrary, Kim et al.[17] and Sousa-Aguiar et al.[36] reported that overall DME direct synthesis can be determined by methanol synthesis rate on the admixed catalyst with metal compositions higher than the optimized one. Clearly getting the balance between functionalities is critical in the design of the overall catalyst. Furthermore the fact that the relative rates of the main reactions change considerably with temperature suggests that this ratio is also strongly related to the operating conditions of the reactor. Recently, Garcia-Trenco et al.[6] studied the effect of the preparation method on the stability of the catalyst and they found that the catalyst prepared by mixing the pre-pelletized components showed high stability with no signs of deactivation over 50 h.

Herein we investigate the activity of admixed catalysts made by combining CZA, for methanol synthesis, and various solid acids (NH$_4$ZSM-5(SiO$_2$/Al$_2$O$_3$=80), HZSM-5 (SiO$_2$/Al$_2$O$_3$=80), NH$_4$ZSM-5(SiO$_2$/Al$_2$O$_3$= 23), γ-Al$_2$O$_3$ and 10% MgOZSM-5(SiO$_2$/Al$_2$O$_3$=80)). The effect of the acid fraction in the CZA/γ-Al$_2$O$_3$ and CZA/HZSM-5(80) admixed catalyst as well as their stability (aging) during storage and under operation are discussed. Within this manuscript we will focus on using a moderate pressure i.e. 20 bar, which is lower than that typically used in industry. The reason of this is that this work forms part of a larger investigation into low temperature distributed DME synthesis and where lower pressures were calculated to improve overall energy efficiency.
2. Experimental

2.1 Catalyst Preparation

2.1.1 Material

The chemicals used in the present study were all analytical grade and supplied by Aldrich, UK. These included copper nitrate \([\text{Cu(NO}_3\text{)}_2 \cdot 2.5\text{H}_2\text{O}]\), zinc nitrate \([\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}]\), aluminum nitrate \([\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}]\) and sodium carbonate \([\text{Na}_2\text{CO}_3]\).

2.1.2 CuO/ZnO/Al\(_2\)O\(_3\) Catalyst

The CuO/ZnO/Al\(_2\)O\(_3\) catalyst was prepared by a conventional co-precipitation method with a wt% ratio of CuO:ZnO:Al\(_2\)O\(_3\)=60:30:10 (BET =56.9 m\(^2\)/g, pore size=1.05 nm). The mixed solutions of copper, zinc and aluminum nitrate and an aqueous solution of Na\(_2\)CO\(_3\) were added drop wise to a beaker contains deionized water, under continuous mixing at 70 °C. The pH was adjusted to seven during precipitation by controlling the flow rates of two solutions. After precipitation, the precipitate was aged for 1 hr 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 simplicity this catalyst is referred to herein as CZA.

2.1.3 Solid Acid Catalysts

The \(\gamma\)-Al\(_2\)O\(_3\) (BET = 117 m\(^2\)/g, pore size=1.035 nm) acid function was prepared by crushing \(\gamma\)-Al\(_2\)O\(_3\) pellets (Alfa Aesar). Commercial NH\(_4\)-ZSM-5 zeolite (Alfa Aesar) with (SiO\(_2\)/Al\(_2\)O\(_3\)=80 or 23) were also used, both have BET of 425 m\(^2\)/g with an
average pore size=1.6 nm. 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 a homogenous mixture, the resultant powder was pressed into tablets and then crushed and sieved to particles of 0.25-0.425 mm (in diameter).

2.2 Catalysts Activity for DME Synthesis
DME synthesis was carried out in an isothermal fixed bed reactor made of stainless steel with an inner diameter of 6 mm placed in ceramic tubular furnace controlled by a Eurotherm2604 PID controller. Typically 250 mg of the catalyst in the form of pellets (250-425 µm) was placed in the reactor. The catalyst bed temperature was measured with a K-type thermocouple placed in the centre. The pressure of the reactor was controlled by means of back pressure regulator and the syngas flow rate was controlled by a mass flow controller (Bronkhorst UK Ltd). Before the reaction the catalyst was activated in situ with 20 ml/min (5% H₂/He) at 250 °C for 6 h at atmospheric pressure.

The typical composition of the syngas used in the methanol synthesis is H₂:CO ratio of 2:1 with 1-4% CO₂ (this gas composition was found to give the best results for the present reaction [37]). Therefore after activation the catalyst was exposed to the syngas mixture (BOC gases) which contained (62% H₂, 31% CO, 4% CO₂ and 3% Ar) [38, 39]. The activity tests were carried out in a temperature range of 200 to 260
°C, at 20 bar and a space velocity of syngas mixture of 2400 ml.h⁻¹.g⁻¹.cat. On-line analysis of the reactants and products were performed using a Perkin Elmer; Clarus 500 Arnel valved gas chromatograph, equipped with a thermal conductivity detector (TCD) and a Flame Ionisation Detector (FID). A Hayesep D column was used for the separation of CO, CO₂, DME, MeOH, CH₄, C₂H₄, C₂H₆, ethanol, propanol, and butanol. The equipment setup used in this study is represented in Figure 1.

The CO conversion ($X_{CO}$) Eq. 5 was calculated based on the molar flow rate of CO in the feed ($F_{CO,in}$) and in the outlet stream ($F_{CO,out}$):

$$X_{CO} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \quad (5)$$

The selectivity to DME ($S_{DME}$) was determined in Eq. 6 as the ratio (expressed in mole%) between the content of carbon in the product DME and the sum of carbon contents corresponding to all the products formed that are present in the reactor outlet stream:

$$S_{DME} = \frac{2F_{DME}}{F_{CO2} + F_{MeOH} + 2F_{DME} + \sum_{i} n_{C_i} F_{i}} \quad (6)$$

or it can also be calculated as the ratio (expressed in mole%) between the content of carbon in the product DME and the sum of carbon contents corresponding to the organic products formed that are present in the reactor outlet stream, see Eq. 7:
\[ S_{\text{DME}} = \frac{2F_{\text{DME}}}{F_{\text{MeOH}} + 2F_{\text{DME}} + \sum n_{Ci}F_i} \]  \hspace{1cm} (7)

where \( F_{\text{DME}}, F_{\text{CO2}} \) and \( F_{\text{MeOH}} \) are the molar flow rates of DME, CO\(_2\) and MeOH in the outlet stream, respectively, \( n_{Ci} \) is the number of carbon atoms for each of the hydrocarbons (byproducts) and \( F_i \) is the molar flow rate of these hydrocarbons [39].
2.3 Catalyst Characterization

Powder X-ray diffraction (XRD) experiments of the catalysts were carried out using a PANalytical X’Pert Pro X-ray diffractometer. This diffractometer is equipped with a CuKα X-ray source with wavelength of 1.5405 Å. A typical experiment entailed using the spinner PW3064 (ex-situ) and Anton Parr (in-situ). The diffractograms were collected from 10° to 89°, with a step size of 0.0167 ° and a scan speed of 0.2089 ° s\(^{-1}\). The X-ray detector was set at 40 kV and 40 mA. Once the scan had finished, the main peaks were selected and compared to diffraction patterns in the software library. The pattern with the highest percentage match is usually the pattern which the sample was matched against.

The acidity of the samples was measured by NH\(_3\)-TPD. This was performed using 50 mg of the catalyst after pretreatment at 500 °C for 90 min in a 50 ml/min of 10% O\(_2\)/He or 5% H\(_2\)/Ar flow. The sample was saturated with NH\(_3\) for 30 min at 150 °C. After saturation, the sample was purged with He for 45 min to remove any physically adsorbed NH\(_3\). The temperature of the sample was then raised from 150 to 700 °C at 10 °C min\(^{-1}\) with the gas stream analysed using a TCD detector.

The reducibility of the catalysts was investigated using a Temperature-programmed reduction (TPR) technique. All the TPR experiments were performed on a Micromeritics Autochem 2910 apparatus and the H\(_2\) uptake was monitored by a TCD from -50 to 700 °C at 10 °C min\(^{-1}\) under flowing 5% H\(_2\)/Ar. Before TPR analysis, all the samples were pretreated at 500 °C under flowing 10% O\(_2\)/He, and then the temperature was decreased to -50 °C under flowing Ar before initiating the TPR experiment.
Temperature-programmed oxidation (TPO) experiments were performed for the used catalyst (after reaction). The products from TPO were monitored by using Hiden™ HPR-20 mass spectrometer from 25 to 850 °C under flowing 10% O₂/Ar.

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

3. Results and Discussion

3.1 Catalyst characterization

3.1.1 Characterization of CZA catalyst

Figure (2) show the in situ XRD patterns of the CZA catalyst during reduction under 5% H₂/He at 250 °C for 6 hrs. The result obtained suggests the presence of a CuO phase (2θ = 35.2, 38.5°). Very weak reflections due to the ZnO phase (2θ = 31.8, 36.2°) and the CuO and ZnO peaks are not finely resolved. The broad reflections indicate that part of the copper may be dissolved in the Zn matrix or that the CuO phase is in intimate contact with the ZnO phase[40]. Reflections due to Al₂O₃ could not be observed. This is due to the fact that the Al₂O₃ phase may be in the amorphous state. The CuO peaks in the fresh catalyst disappeared after one (1) hour exposure to the gas mixture and metallic Cu became the main phase while ZnO remains unchanged and hence ZnO peaks are resolved from CuO peaks. However, diffraction lines due to ZnO in the used form are predominant and broad when compared to the fresh calcined samples, where poorly crystalline peaks are observed. Reflections attributed to γ-Al₂O₃ peaks, in weak intensity, could be seen over the reduced catalysts. The peaks at 43.4 and 50.3° of the reduced catalyst are attributed to
metallic copper [41]. It is also seen that there is no change of XRD patterns with time of exposure of the catalyst to H₂, indicating that the CZA catalyst is easy to reduce.

The size of ZnO and CuO crystallites in the catalyst precursor after calcination was 7 nm, as estimated from ZnO(100) and CuO(111) XRD peak widths.[42]

3.1.2 Admixed Catalyst Characterization

3.1.2.1 Temperature Program Reduction (TPR)

Figure (3) shows the TPR for the admixed catalysts. All the admixed catalysts had metal to acid ratio of 2. 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. It can be seen that all the catalysts have the same peak intensity during the same period of time. Table (1) shows the effect of the physical mixing of different solid acid functions on the reductive properties of CZA. All the admixed catalysts used had the same amount of CZA (in the form of pure CZA catalyst). The actual amount of H₂ consumed by the catalyst was calculated from the area of the corresponding peak.

Assuming that all the Cu (47 %) in the CZA catalyst is present as CuO (as suggested by the XRD for CZA), the theoretical amount of H₂ consumed for the complete reduction of CuO (H₂/CuO ~ 1) is 7.5 mmol H₂ per gram of CZA catalyst (or 15.7 mmol H₂ per gram of Cu in CZA catalyst). Table (1) shows that the H₂ consumption for all samples of admixed catalyst is the same i.e. 11.48 mmol per gram of Cu. For the pure acid catalyst i.e. NH₄ZSM5 (80) the hydrogen consumption was 0.013 mmol per gram of catalyst, which means that the acid solid fraction is not reducible as
expected. The actual amount of $H_2$ consumed is less than the theoretical amount for complete reduction of CuO to Cu$^0$. Therefore, it appears not all of the CuO exists in Cu$^0$ phase or is accessible to hydrogen.

3.1.2.2 NH$_3$-Temperature Program Desorption (NH$_3$-TPD)

Figure (4) shows the NH$_3$-TPD profiles of desorption of the solid acid catalysts for the fresh and reduced forms. It is clear that there is no difference between the reduced and unreduced phase for all acid solid catalysts which is in agreement with the TPR results. With the exception of $\gamma$-Al$_2$O$_3$ each profile shows two distinct regions. The peak at 250-350 °C corresponds to the weak acid sites whereas the peak at higher temperature around 450-550 °C are attributed to the strong acid sites [5, 43]. It is clear that the high temperature peak intensity increased as SiO$_2$/Al$_2$O$_3$ decreased. This was again attributed to the increase in aluminium both in the framework and in extra-framework position [44]. It can be seen also that, with the decrease of SiO$_2$/Al$_2$O$_3$, the desorption temperature of NH$_3$ from the strong acid sites shifted to higher temperature which strongly suggests the existence of aluminum in extra-framework positions which is in agreement with Shirazi et al.[44]. Xu et al.[4] proved that for low (SiO$_2$/Al$_2$O$_3$) ratio in HZSM-5, the Brønsted (strong) and Lewis (weak) acid sites play a role in the methanol dehydration reaction and as the ratio increased, the solid acid exhibits only strong acid sites since there is no extra-framework aluminum. As shown Figure (4), the area below the TPD curves indicates that the total number of acid sites on the surface of the catalyst [3] decreases in the order of HZSM- 5(23) > HZSM-5(80) > $\gamma$-Al$_2$O$_3$. An additional conclusion which may be drawn from these results that the operating conditions of the reactor used
here would be insufficient to be able to desorb any strongly bound basic compounds from the HZSM-5 catalysts.

3.2 Catalyst activity testing

3.2.1 CZA catalyst activity

Figure (5) reports the CO conversion for CZA at 20 bar as well as theoretical equilibrium conversion. It is clear that the CZA catalyst was active at high temperatures and that the CO conversion ($X_{CO}=20.5\%$) obtained approached the theoretical equilibrium conversion ($X_e=21.3\%$) at 250 °C and 20 bar. It was however far away ($X_{CO}=12.6\%$) from equilibrium ($X_e=60.8\%$) at 200 °C and 20 bar.

3.2.2 DME Synthesis

Table (2) shows the effect of temperature (205 and 260 °C) on the activity for different admixed catalysts. All the admixed catalysts in the table were prepared by physically mixing the CZA and solid acid components; here the metal to acid ratio was kept at a constant value of two. As shown in Table (2) there is an insignificant difference in DME production rate for the admixed catalysts containing acid function $\text{NH}_4\text{ZSM-5}(80)$, HZSM-5 (80) and $\text{NH}_4\text{ZSM-5}(23)$ at 260 °C. As a consequence, and under these conditions, the overall one step DME synthesis is controlled by the methanol synthesis reaction. The percentages of DME produced for the admixed catalysts containing acid function with $\gamma$-$\text{Al}_2\text{O}_3$ and 10% MgOZSM-5(80) are less than 5% and 1%, respectively. Such a decrease in the DME production is related to the mild acidity of $\gamma$-$\text{Al}_2\text{O}_3$ and weak acidity of 10% MgOZSM-5(80). Hence under these conditions, the overall one step DME synthesis is controlled by the methanol dehydration reaction. It is also clear that the concentration of methanol increased as the strength of the acid function decreased which confirms that the rate limiting step
of weak acids is the methanol dehydration reaction. Mao et al.[45] studied the effect of the modification of HZSM-5 zeolites with MgO (0-10 wt%) and then physically admixed these with CZA to form admixed catalysts. They found that the hybrid catalyst containing the MgO with 10 wt% exhibited the lowest selectivity for DME and the highest selectivity for methanol due to its low acidity, which is in agreement with our results. Naik et al.[46] compared two different bifunctional hybrid DME synthesis catalysts, CZA/Al₂O₃ and CZA/HZSM-5 for CO₂ hydrogenation to DME. They found that the CZA/HZSM-5 showed higher activity.

From Table (2), it can be seen that ethylene was formed when the temperature increased from 200 to 260 °C. This was expected as DME dehydration occurs at such temperatures. It can also be seen that the amount of by products (ethylene and others) for all admixed catalyst mentioned above are negligible. The synergetic effect of combining the metal and acid function can be seen by comparing the conversion of CO in the methanol synthesis catalyst with the admixed catalyst of DME synthesis which increased from 20.6 % to around 63 %.

3.2.2.1 Effect of Acid Fraction in Admixed Catalyst

As shown above for the one step DME synthesis a balance must be obtained between the two main catalytic functions. The net acidic function can be modified either through adjusting the acid strength or the quantity of acid sites. For the former there is an increasing risk of by-product formation while the latter requires a larger amount to be used. Therefore an appropriate ratio of metal to acid function should be chosen. Many researchers have studied the effect of the acid fraction in bifunctional catalysts
In the present study, and in order to estimate the optimum ratio, two admixed catalysts with different metallic to acid function ratio were studied.

3.2.2.1.1 CZA/γ-\(\text{Al}_2\text{O}_3\)

As can be seen from Table (3a) all catalysts exhibited low activity regardless the metal:acid ratio, this could be due to the low reaction temperature (i.e. 260 °C). Fu et al. [8] and Jiang et al. [3] studied the effect of temperature on the activity of γ-\(\text{Al}_2\text{O}_3\) for dehydration of methanol to DME. They found that γ-\(\text{Al}_2\text{O}_3\) exhibited low activity at temperatures below 300 °C, however as discussed previously temperatures >300°C lead to sintering of the CZA. As shown for a 3:1 ratio, the DME concentration is low and methanol concentration is high which means that the amount of acid is insufficient to convert the methanol formed to DME. In this case, the methanol dehydration reaction is the rate limiting step. For 1:1 and 2:1, the DME (mole %) formed at 260 °C is 5.5 mole % (54.19 % yield ) and 4.8 mole % (46.45 % yield ), respectively. The results reported in Table (3a) also showed that as the acid fraction in the admixed catalyst increased the amount of methanol converted to DME is also increased, with a maximum for 0.5 acid fraction corresponding to the maximum ratio tested. It is clear that there is no significant difference between 0.33 and 0.5 acid fraction, which means there are no benefits in increasing the acid fraction more than 0.5, particularly once the excess acid starts converting the DME to other byproducts under these conditions, which is in agreement with the tests using commercial CZA catalyst[2].
3.2.2.1.2 CZA/HZSM-5(80)

In Table (3b) the effect of the HZSM-5(80) fraction in the admixed catalyst on mole % of MeOH, mole % of DME and % yield of DME is observed. It is clear that the methanol concentration is low for all ratios, which means that almost all the MeOH formed is converted to DME. In this case, the MeOH synthesis reaction is the rate limiting step. As seen, at low temperature (200 °C) all the catalysts produced the same amount of DME, when the temperature increased to 260 °C, side reactions take place and some of DME starts converting to ethylene. The maximum DME production is 10.7 % (100 % yield) at the 3:1 ratio. The amount of ethylene formed at 260 °C for 0.25, 0.33 and 0.5 acid fraction is 0.01%, 0.02% and 0.09%, respectively. It is clear that ethylene increases with acid fraction. For the 1:1 ratio (0.5 acid fraction), the amount of zeolite is larger than that required to convert the MeOH to DME, therefore the excess amount of zeolite has a higher probability to convert the DME to other by-products.

From Table (3b), it can be seen also that the admixed catalyst with a low fraction of zeolite showed a high production of DME. Similar results have been attributed to rate limiting step being the methanol synthesis[17], and as a consequence it is desirable to increase the fraction of catalyst function responsible for the methanol synthesis. As reported by Kim et al.[17] overall DME direct synthesis can be determined by the methanol synthesis rate on the admixed catalyst with metal compositions higher than the optimized one and the overall rate can be controlled by the methanol dehydration rate on the admixed catalysts with metal composition lower than the optimized one. Here a relatively small amount of acid sites were sufficient to convert methanol into DME as the rate of dehydration due to HZSM-5
(80) is much faster than the methanol formation rate (rapid transformation of methanol to DME). Wang et al.[48] used two kinds of HZSM-5 zeolite in the STD at different ($\text{SiO}_2/\text{Al}_2\text{O}_3$) ratio with CuO/ZnO/Al$_2$O$_3$. They found that the acidity of HZSM-5 played a critical role in the performance of STD catalyst, and that an optimal acidic amount was required to obtain the best activity of STD catalyst; more and less acidic amounts were both unfavourable for DME.

From Table (3) we can identify the best ratio, from those tested, of CZA/ acid catalyst for DME synthesis from syngas for CZA/ $\gamma$-$\text{Al}_2\text{O}_3$ and CZA/HZSM-5(80) are 1:1 and 3:1, respectively. Again this demonstrates that the relative difference in acidity between the two acid catalysts at the operating conditions mentioned above which is in agreement with the tests using commercial CZA catalyst[2]. From the data given here and in the literature it is possible to estimate the relative rates of reaction for the various catalysts tested. Table (4) shows the reaction rates of methanol synthesis (Eq.1) and the effect of the acid catalyst on DME formation from methanol (Eq.2). It is clear for HZSM-5 acid catalysts that as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increased the DME formation rate decreased. It can be also be seen that the rate of DME formation deceased as the acidity of the acid catalyst decreased in order of $\gamma$-$\text{Al}_2\text{O}_3 < \text{HZSM-5}(140) < \text{HZSM-5}(80) < \text{HZSM-5}(50) < \text{HZSM-5}(30)$.

From this data one can use a simple ratio to determine how much of each catalyst would be required in order to match the two reaction rates. (see the supplementary data).

From Figure (S1) and (S2) (see the supplementary data), the optimum ratio of CZA/ acid catalyst for DME synthesis from syngas for CZA/ $\gamma$-$\text{Al}_2\text{O}_3$ and CZA/HZSM-
5(80) are 1.1 (i.e. acid fraction of 0.462) and 3.12 (i.e. acid fraction of 0.235), respectively, further confirming the results presented in Table (3).

3.2.2.2.3 Admixed Catalyst Stability on storage

Catalyst stability is a crucial parameter for future applicability of the catalyst in this reaction. Table (5) reports the activity results obtained for admixed catalyst for DME synthesis using different acid functions stored for different length of (at room temperature in a closed container). The DME to methanol ratio decreases with storage time but in different ratios and the decrease corresponds to a similar increase in the mol% of MeOH. This indicates that the acidic component of the admixed catalyst has deactivated more than that of the sites for methanol formation. It can also be seen that the mol% of DME obtained is a function of acid used. CZA/NH₄ZSM5 (80) catalyst lost 23% of its initial activity (with respect to the fresh catalyst) after 2 weeks of storage and 64% after 2 months. Furthermore one can conclude that the operating conditions of the reactor are insufficient to reactivate the acidic component of this mixed catalyst system.

Furthermore the CZA/γ-Al₂O₃ catalyst lost 36% of its initial activity (as compared to the fresh catalyst) after one month of storage while it can be seen that CZA/ HZSM5 (80) catalyst lost 9.8% of its initial activity after one month which is within error margin of these experiments. As a conclusion, it is clear that HZSM5 (80) based catalysts is the more stable catalyst with respect to storage. This loss may be attributed to zeolitic water adsorbed at the surface of the acid function but could also be due to other more strongly adsorbed basic molecules as discussed in section 3.1.2.2.
3.2.2.1.3 Catalyst Stability on stream

In order to investigate the stability of the admixed catalyst, an admixed catalyst containing the CZA-HZSM5 (80) combination with a metal:acid ratio=3:1 was evaluated over a 212 h (~ 9 days), in which the reactor was operated continuously under steady state reaction conditions. The changes of mol% DME, mol% MeOH and selectivities of the main products as function of time are represented in Figure (6) and Figure (7), respectively. It is clear that DME and methanol follow the same trend, as shown in Figure (6). DME production and MeOH production at 260 °C decreased from 10.5 % to 8.8 % and from 0.68 % to 0.58 %, respectively, which means that the admixed catalyst deactivated and lost around 16.2 % of its initial activity in the case of DME and 14.7 % of its initial activity in case of methanol. The possible causes of deactivation are coke deposition on the active sites of the metallic and acid functions, as well as sintering of the metallic function. Furthermore, water in the reaction medium may be responsible for the decrease in the activity of the acid sites [49], although this is unlikely to be the major source of deactivation given the DME production rate.

As shown in Figure (7) % selectivity (calculated using Eq. 7) of DME and other products remained constant over a period of 212 hrs (~ 9 days), the selectivity for DME was 69 mol% based (on all products, i.e. Eq. 7) and 99 mol% (based on organic products, i.e. Eq. 6).

Figure (8) shows the product distribution of direct DME synthesis over CZA/HZSM5 (80) 3:1 ratio catalyst. It can be seen that the main products are DME, MeOH and
CO\textsubscript{2} with mol\% of 53.5, 3.5 and 43 \% at 260 °C and 50.1, 4.5 and 45.5 at 200 °C, respectively. It can be also seen that the ratio of DME/CO\textsubscript{2} was (~1.1-1.25), which means that under the conditions used in direct DME synthesis, the overall process follows below reported reaction:

\[ 3\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2 \]

Figure (9) reports the TPO curve obtained with a CZA/HZSM-5(80) with metal:acid ratio =3:1 after exposure to the same reaction conditions of Figure (6). 3 main peaks can be observed; a low temperature peak (predominant peak) was attributed to the removal of homogeneous coke deposited on the sites of the metallic function [49]. The combustion of this coke takes place at 159 °C, catalyzed by the metallic function itself. The second peak corresponds to the combustion of part of the coke which requires a higher temperature (peak at 447 °C), as it is deposited on the Al\textsubscript{2}O\textsubscript{3} support of the CZA and its combustion is not activated by the presence of metallic sites. The third peak at high temperature (at 818 °C) was attributed to graphitic coke deposited on the support and whose combustion cannot be catalyzed by metallic sites [50]. These results are consistent with literature data showing that there are three different types of coke: (1) a peak at low temperature, corresponding to the coke deposited on the metallic sites; (2) a peak at intermediate temperature, corresponding to the coke deposited on the interface between the metallic sites and the support near the metal-support; and (3) high temperature peak corresponds to graphitic coke deposited on the support which cannot be catalyzed by metallic centers [49, 50].

The results reported in Figure (6) (long time study of CZA/HZSM5) and those in Figure (9) (TPO) are herein explained by catalyst deactivation due to coke which
hinders the route for methanol formation. Based on the TPO results this coke formation is attributed to the degradation of methoxy ions (to which the dehydrogenating capacity of the metallic function for activating condensation steps will contribute), dehydrocyclization, and aromatic condensation steps [51].

4. Conclusion

Herein different acid solid catalysts were studied as a dehydration component in direct DME synthesis (NH₄ZSM-5 (SiO₂/Al₂O₃=23, 80), HZSM-5 (SiO₂/Al₂O₃=80) or γ-Al₂O₃). From those tested it was found that the HZSM-5 catalyst has the most stable acid function when considering overall application including long term storage. Furthermore the HZSM-5 catalyst also possessed a high activity for the dehydration reaction at relatively low temperature compared with γ-Al₂O₃ as expected.

The effect of acid fraction in the admixed catalyst was also studied. Under the conditions used here the most suitable ratio between the metal and acid function was 1:1 for CZA/γ-Al₂O₃ and 3:1 for CZA/ HZSM-5 admixed catalyst. Moreover, the stability of the CZA/ HZSM-5 with a ratio of 3:1 was studied over a continuous period of 212 hr (~9 days) the results showed that the selectivity of DME keep constant over all the period.

The catalyst was however observed to slowly deactivate due to the formation of coke on the surface of the catalyst. Hence it was the deactivation of MeOH synthesis step which led to the overall deactivation of the mixed catalyst system. The temperatures required to remove this coke are greater than the sintering temperature of the catalyst.
References:


Figure (1): DME Equipment setup.
Figure (2): in situ XRD patterns of CZA catalyst during reducing treatment by 5% H\textsubscript{2}/He at 250 °C for 6 hrs. (a fresh catalyst, (b after 1 hr of reduction, (c after 2 hr of reduction, (d after 3 hr of reduction, (e after 4 hr of reduction, (f after 5 hr of reduction and (g after 6 hr of reduction.
**Figure (3):** TPR patterns for the admixed catalyst.
Figure (4): Comparison of NH₃-TPD profiles of reduced and unreduced solid acid catalysts.
Figure (5): Comparison of theoretical equilibrium conversion and experimental CO conversion for CZA at 20 bar. The catalyst was reduced in 5% H₂/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g⁻¹ h⁻¹.
Figure (6): long term test of DME and MeOH production of the admixed catalyst CZA/HZSM5 (80) with time, metal:acid ratio=3:1. The catalyst was reduced in 5% H₂/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g⁻¹ h⁻¹.
Figure (7): long term test of the selectivity (calculated using Eq. 7) of the admixed catalyst CZA/HZSM5 (80) with time, metal:acid ratio=3:1. The catalyst was reduced in 5% H$_2$/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g$^{-1}$ h$^{-1}$.
Figure (8): Product distribution on CZA/HZSM5 (SiO2/Al2O3=80) 3:1 ratio catalyst at 20 bar. The catalyst was reduced in 5% H₂/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g⁻¹ h⁻¹.
**Figure (9):** TPO curve of coke deposited on CZA/HZSM-5(80), 3:1 ratio. The catalyst treated under flowing 10% O₂/Ar.
Table 1
Temperature programmed Reduction data for CuO/ZnO/Al₂O₃ and admixed catalysts. Before analysis, all the samples were pretreated at 500 °C under flowing 10% O₂/He.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂ consumption mmol H₂/g catalyst</th>
<th>H₂ consumption mmol H₂/g CZA catalyst (mmol H₂/g Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA¹</td>
<td>5.5</td>
<td>5.5 (11.48)</td>
</tr>
<tr>
<td>NH₄ZSM5(80)² zeolite</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>CZA/NH₄ZSM5(23)³, 2:1 ratio⁴</td>
<td>3.7</td>
<td>5.5 (11.48)</td>
</tr>
<tr>
<td>CZA/NH₄ZSM5(80), 2:1 ratio⁴</td>
<td>3.7</td>
<td>5.5 (11.48)</td>
</tr>
<tr>
<td>CZA/HZSM5(23), 2:1 ratio⁴</td>
<td>3.7</td>
<td>5.5 (11.48)</td>
</tr>
<tr>
<td>CZA/HZSM5(80), 2:1 ratio⁴</td>
<td>3.7</td>
<td>5.5 (11.48)</td>
</tr>
<tr>
<td>CZA/10% MgOZSM5(80), 2:1 ratio⁴</td>
<td>3.7</td>
<td>5.5 (11.48)</td>
</tr>
</tbody>
</table>

¹: CZA is CuO/ZnO/Al₂O₃
²: (80) is SiO₂/Al₂O₃ molar ratio=80
³: (23) is SiO₂/Al₂O₃ molar ratio=23
⁴: metal to acid weight ratio= 2:1
Table 2
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 (wt. ratio)*.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(X_{CO} ) (%)</th>
<th>DME (mole %)</th>
<th>MeOH (mole %)</th>
<th>(C_2H_4) (mole %)</th>
<th>(CO_2) (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>205 °C</td>
<td>260 °C</td>
<td>205 °C</td>
<td>260 °C</td>
<td>205 °C</td>
</tr>
<tr>
<td>CZA/NH4ZSM-5(80)</td>
<td>6.38</td>
<td>63.43</td>
<td>1</td>
<td>10.8</td>
<td>0.19</td>
</tr>
<tr>
<td>CZA/NH4ZSM-5(23)</td>
<td>4.72</td>
<td>59.24</td>
<td>0.84</td>
<td>9.6</td>
<td>0.11</td>
</tr>
<tr>
<td>CZA/HZSM-5(80)</td>
<td>3.97</td>
<td>59.77</td>
<td>0.77</td>
<td>10</td>
<td>0.06</td>
</tr>
<tr>
<td>CZA/(\gamma)-Al_2O_3</td>
<td>12.24</td>
<td>37.74</td>
<td>0.24</td>
<td>4.6</td>
<td>4.3</td>
</tr>
<tr>
<td>CZA/10% MgOZSM-5(80)</td>
<td>10.18</td>
<td>19.76</td>
<td>0.033</td>
<td>0.64</td>
<td>4.2</td>
</tr>
<tr>
<td>CZA</td>
<td>12.6</td>
<td>20.5</td>
<td>0</td>
<td>0.02</td>
<td>4.3</td>
</tr>
</tbody>
</table>

*: The catalyst was reduced in 5% H\_2/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g\(^{-1}\) h\(^{-1}\).
Table 3a
Effect of acid fraction in CZA/\(\gamma\)-\(\text{Al}_2\text{O}_3\) catalyst on the amount of methanol and DME produced at 20 bar.

<table>
<thead>
<tr>
<th>CZA/(\gamma)-(\text{Al}_2\text{O}_3)</th>
<th>Acid weight fraction</th>
<th>200 °C</th>
<th>260 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeOH mole %</td>
<td>DME mole %</td>
</tr>
<tr>
<td>3/1</td>
<td>0.25</td>
<td>3.84</td>
<td>0.062</td>
</tr>
<tr>
<td>2/1</td>
<td>0.33</td>
<td>4.3</td>
<td>0.25</td>
</tr>
<tr>
<td>1/1</td>
<td>0.5</td>
<td>3.94</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 3b
Effect of acid fraction in CZA/HZSM-5(80) catalyst on the amount of methanol and DME produced at 20 bar.

<table>
<thead>
<tr>
<th>CZA: HZSM-5(80)*</th>
<th>Acid weight fraction</th>
<th>200 °C</th>
<th>260 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeOH mole %</td>
<td>DME mole %</td>
</tr>
<tr>
<td>3/1</td>
<td>0.25</td>
<td>0.064</td>
<td>0.72</td>
</tr>
<tr>
<td>2/1</td>
<td>0.33</td>
<td>0.061</td>
<td>0.77</td>
</tr>
<tr>
<td>1/1</td>
<td>0.5</td>
<td>0.049</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*: The catalyst was reduced in 5% \(\text{H}_2/\text{He}\) @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g\(^{-1}\) h\(^{-1}\).
Table 4
Effect of the catalyst on reaction rate at 260 °C, P=20 bar for MeOH synthesis and P=1 bar for MeOH dehydration.

<table>
<thead>
<tr>
<th></th>
<th>Reaction rate mmol g-cat(^{-1}) hr(^{-1})</th>
<th>MeOH synthesis</th>
<th>DME formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA(^1)</td>
<td>30.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HZSM-5 (30)(^2)</td>
<td>-</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>HZSM-5 (50)(^3)</td>
<td>-</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>HZSM-5 (80)(^4)</td>
<td>-</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>HZSM-5 (140)(^5)</td>
<td>-</td>
<td>43.1</td>
<td></td>
</tr>
<tr>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>17.5</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\): CZA is CuO/ZnO/Al\(_2\)O\(_3\)
\(^2\): (30) is SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio=30
\(^3\): (50) is SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio=50
\(^4\): (50) is SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio=80
\(^5\): (50) is SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio=140
Table 5
Effect of storage on the stability of the admixed catalyst for DME synthesis at 20 bar and metal to acid ratio is 2 (wt. ratio). *

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>time</th>
<th>200 °C</th>
<th>200 °C</th>
<th>200 °C</th>
<th>200 °C</th>
<th>200 °C</th>
<th>200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH mole %</td>
<td>DME mole %</td>
<td>DME/MeOH ratio</td>
<td>MeOH mole %</td>
<td>DME mole %</td>
<td>DME/MeOH ratio</td>
<td></td>
</tr>
<tr>
<td>CZA/NH₄ZSM5 (80)</td>
<td>Fresh</td>
<td>0.186</td>
<td>1.02</td>
<td>5.48</td>
<td>0.918</td>
<td>10.72</td>
<td>11.68</td>
</tr>
<tr>
<td></td>
<td>After 2 weeks</td>
<td>1.07</td>
<td>0.67</td>
<td>0.62</td>
<td>1.88</td>
<td>8.31</td>
<td>4.42</td>
</tr>
<tr>
<td></td>
<td>After 2 months</td>
<td>2.67</td>
<td>0.33</td>
<td>0.12</td>
<td>2.67</td>
<td>3.74</td>
<td>1.40</td>
</tr>
<tr>
<td>CZA/γ-Al₂O₃</td>
<td>Fresh</td>
<td>4.34</td>
<td>0.23</td>
<td>0.053</td>
<td>2.87</td>
<td>4.84</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>After 1 month</td>
<td>3.28</td>
<td>0.091</td>
<td>0.028</td>
<td>4.46</td>
<td>3.02</td>
<td>0.67</td>
</tr>
<tr>
<td>CZA/HZSM5 (80)</td>
<td>Fresh</td>
<td>0.062</td>
<td>0.78</td>
<td>12.58</td>
<td>0.645</td>
<td>10.22</td>
<td>15.84</td>
</tr>
<tr>
<td></td>
<td>After 1 month</td>
<td>0.068</td>
<td>0.66</td>
<td>9.70</td>
<td>0.723</td>
<td>9.19</td>
<td>12.71</td>
</tr>
</tbody>
</table>

*: The catalyst was reduced in 5% H₂/He @ 250 °C, catalyst weight: 250 mg, WHSV: 2400 ml g⁻¹ h⁻¹.
Highlights

- Admixed CZA/Acid catalysts tested for activity and deactivation.
- HZSM-5 catalyst has the most stable acid function during the storage.
- HZSM-5 possessed high activity at low temperature compared with other catalysts.
- High stability of the CZA/HZSM-5 catalyst with constant selectivity of DME.