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Statistical analysis of the performance of a bi-functional catalyst under operating conditions of LPDME process

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Abstract

Liquid phase direct synthesis of dimethyl ether (LPDME^{TM}) under various operating conditions (temperature, H_2/CO molar ratio of feed) was conducted in a mechanically agitated slurry reactor system. Each run was monitored for 60 h time on stream (TOS) in order to confirm the high activity and long-term stability of a bi-functional catalytic system (CuO–ZnO–Al_2O_3/H-MFI-90). Statistical experimental design was applied for determining the optimum operating conditions under which the catalytic system shows the highest performance. A significant improvement in the performance of the bi-functional catalyst was observed when the temperature and H_2/CO molar ratio of feed were increased from 200 to 240 °C and 1 to 2, respectively at a constant pressure of 35 bar and GHSV equal to 1100 mLn/(g-cat h). CO conversion was increased from 9.1 mol% at $T = 200\,°C$ and $H_2/CO = 1$ to 79.6 mol% at $T = 240\,°C$ and $H_2/CO = 2$ and the yield and selectivity of DME also increased from 7.11% to 47.05% and 41.57% to 59.96%, (molar basis) respectively. No significant deactivation has been observed during 60 h TOS at different operating conditions. Furthermore, from the main effect plots and response table results, it was concluded that the most effective factor on activity and stability of bi-functional catalytic system is temperature.

Keywords: Bi-functional catalyst; Dimethyl ether; Experimental design; Stability

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1. Introduction

Today, we have two serious problems in relation with the use of crude oil derived fuels. The first is the limited crude oil reservoirs which encounter with the pressure drop, so the market demand will be higher than oil production in the near future. The second problem is concerned with significant amount of the air pollution such as NO_x, sulfur oxide and non-burned hydrocarbons resulted by using these fuels. Dimethyl ether (DME) cannot only serve as a substitute for diesel as a vehicle fuel due to its high cetane number (55–60), zero content of sulfur, lower NO_x emission, lesser smoke and engine noise but it can also be used as a high-quality household fuel in place of liquefied petroleum gas (LPG). DME is also used as an aerosol propellant because of its environmentally benign properties [1,2]. At the present time, DME is commercially prepared by dehydration of methanol using acidic porous catalysts such as zeolites, silica–alumina, alumina, etc. Recently, an original technique named STD (synthesis gas to dimethyl ether) process was developed for the direct synthesis of DME from synthesis gas (syn gas) in a single reactor on bi-functional catalysts composed of copper-based methanol synthesis catalysts and solid acids. The following main reactions take place simultaneously in the STD process:

- Methanol synthesis reaction:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (1)$$

- Methanol dehydration reaction:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (2)$$

- Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

However, CO_2 takes part in methanol synthesis reaction as: $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ but this reaction can be obtained

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by summation of reactions (1) and (3) and there are only two independent reactions in methanol synthesis reaction. In STD process, all reactions occur on a bi-functional catalyst in a reactor. These reactions form a synergistic system that allows higher synthesis gas conversion per pass in the following manner: methanol produced by reaction (1) which can be at or near its equilibrium value is consumed in reaction (2) for the formation of DME and the water generated in reaction (2) which can limit the rate of reaction (2), is shifted by reaction (3), forming carbon dioxide and hydrogen which in turn are the reactants for methanol synthesis reaction, therefore the products of each step are reactants of the another step [3,4].

Due to synergy effect, thermodynamic restrictions for single pass conversion of synthesis gas is removed and allows very high single pass conversion of synthesis gas (higher productivity) in STD process in comparison with methanol synthesis alone. The slurry phase operation for STD process facilitates heat removal because of higher thermal conductivity and heat capacity of slurry in comparison with a gas, thus enabling isothermal conditions in the reactor system. High agitation rates in the reactor provide a reaction environment devoid of temperature and concentration gradients [4].

One important step for developing this new process is to prepare a bi-functional catalyst with high activity, selectivity and stability which determines the suitability of the catalyst for use in an industrial process.

The aim of this study is to investigate the effect of operating conditions (temperature, H_2/CO molar ratio of feed) on the activity and long-term stability of a bi-functional catalytic system made up of CuO–ZnO–Al_2O_3 and H-MFI-90 zeolite, in the liquid phase dimethyl ether synthesis process from synthesis gas. Furthermore, by using General Factorial Design method to design the experiments and analyze the empirical results, one can see whether there are any interactive or main effects among the specified factors (temperature and feed composition) or not. This statistical investigation is a novel approach for having more systematic understanding of the LPDME processes behavior with changing operation conditions.

2. Experimental

2.1. Catalyst preparation

The bi-functional catalyst for STD process has been prepared by physically mixing the powders of a commercial methanol synthesis catalyst (CuO–ZnO–Al_2O_3, KMT) and a methanol dehydration catalyst, namely H-MFI-90 zeolite with $SiO_2/Al_2O_3 = 90$ mol/mol. Two commercial catalysts were finely ground and sieved to sizes less than 90 μm and then well mixed at mass ratio of metallic function to acidic function of 3:1 [5]. Then the mixture was molded under pressure into tablets, which then were crushed and sieved to 90–120 μm mesh size particles, in order to eliminate the effects of internal diffusion.

2.2. Characterization of catalyst

The BET surface area, pore volume and average pore radius of the catalysts were measured by multipoint N_2 adsorption–desorption isotherm at liquid nitrogen temperature (77 K) using NOVA 2000 Series instrument (Quantachrome, USA). Prior to the analysis, 20 mg of the catalyst was degassed at 150 °C for 16 h under flowing of nitrogen.

Temperature-programmed reduction (TPR) of the catalysts was carried out in a stream of 5.1 vol.% H_2 balanced with Ar at a flow rate of 50 ml/min using a Pulse Chemisorb 2705 instrument (micromeritics, USA). A catalyst sample (20 mg) was placed in a quartz tube and pretreated at 120 °C with N_2 flow of 30 ml/min for 2 h and then cooled to room temperature. After the stream was switched from N_2 to reducing gas, the sample was heated by increasing the temperature linearly at a rate of 5 °C/min. Water which formed during the reduction process was trapped by cooling with mixture of ethylene glycol and liquid nitrogen. The hydrogen concentration in the effluent was continuously monitored by a thermal conductivity detector (TCD).

Acidity measurement was performed by temperature-programmed desorption of ammonia (NH_3-TPD) with a conventional flow apparatus which included an on-line thermal conductivity detector (TCD). In a typical analysis, NH_3-TPD was performed using 0.35 g of the catalyst which was degassed at 600 °C in a helium flow, cooled to 150 °C and then saturated with NH_3 for 15 min. After saturation, the sample was purged with He for 30 min to remove weakly adsorbed NH_3 on the surface of the catalyst. During this time, a constant TCD level was attained. The temperature of the sample was then raised at a heating rate of 5 °C/min from 150 to 700 °C and the amount of ammonia in effluent was measured via TCD and recorded as a function of temperature.

Chemical compositions of the catalysts were determined by X-ray fluorescence (XRF). A PW-1800 Philips X-ray fluorescence has been used for elemental analyzing. X-ray powder diffraction (XRD) measurements were performed on a PW-1800 Philips X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å, 45 kV, 40 mA).

2.3. Catalyst activity test

A schematic view of the lab-scale setup was depicted in Fig. 1. In the feeding section, the reactants CO (purity, 99.99%), H_2 (purity, 99.99%) and the internal standard nitrogen (purity, 99.99%) were fed through a set of mass flow controllers (Brooks models 5850E & 5850S). After passage through mass flow controllers, the three gases were blended. Blended gas from mixer was passed over ZnO guard to remove any trace poisons, such as metal carbonyls. The gas mixture was preheated to the reaction temperature before entering the reactor. The catalyst activity and stability test by direct DME synthesis reaction was carried out in a 1 L mechanically agitated slurry reactor, equipped with four bladed impeller and withstanding temperatures up to 300 °C and pressures up to 100 bar, in which the 10.5 g bi-functional catalyst was suspended in 350 g pure liquid paraffin (treated to remove any trace poisons before use) with boiling point of higher than 305 °C. The reaction pressure was maintained with a back pressure regulator (BPR, model 5866 Brooks). The down line effluent was constantly kept at temperatures over 100 °C, to avoid possible condensation of some components in the product

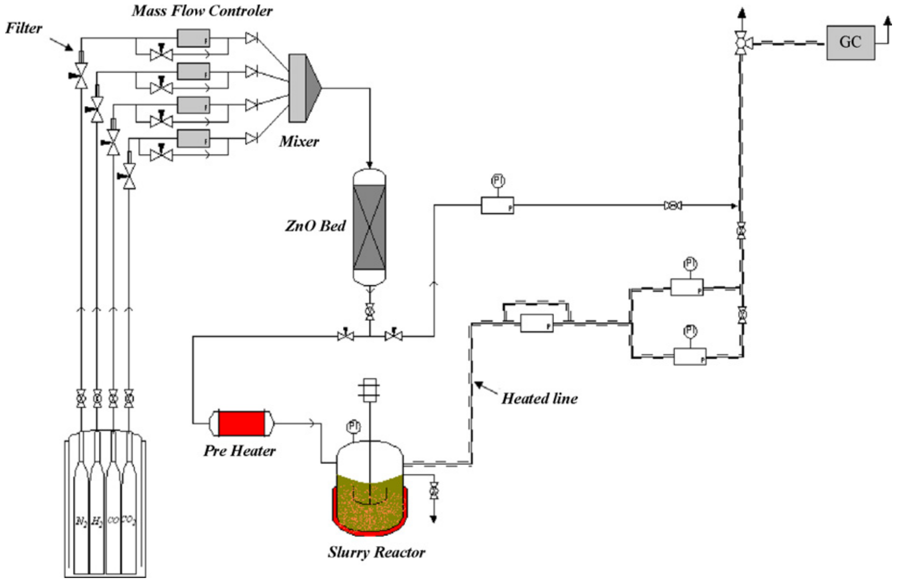

Fig. 1. Schematic view of the experimental setup.

gas such as water or methanol. Before each activity test, the bi-functional catalyst was reduced with a hydrogen stream diluted in nitrogen (at 10 vol.%) at the normal pressure according to the following heating program: heated from room temperature to 250 °C with heating rate of 1 °C/min and was kept for 6 h at this temperature. Then, the catalyst was cooled to room temperature at the presence of hydrogen flow. After this pre-treatment, the syn gas (H_2 + CO with N_2 as balance gas) was introduced into the autoclave reactor. The outlet stream of reactor passed through the back pressure regulator where its pressure was reduced to atmospheric pressure and then a small fraction of it was piped to a Varian CP-3800 gas chromatograph (GC) in order to on line analysis. Gas chromatograph was equipped with two packed columns: HaySep Q (80–100 mesh, 2 m × (1/8) in. × 2.0 mm, SS) for separating CO_2, H_2, N_2, CO and Chrompach Molecular Sieve 13X (80–100 mesh, 2 m × 1/8 in. × 2.0 mm, SS) for separating MeOH, DME, CH_4 and C_3H_8 and then detecting by a thermal conductivity detector (TCD). By using the obtained chromatograph results of the outlet gas, the conversion of CO (X_{CO}), DME selectivity (S_{DME}) and the yield of DME (Y_{DME}) can be calculated as follows [6]:

$$X_{CO} = \frac{F(y_{CO})_{in} - P(y_{CO})_{out}}{F(y_{CO})_{in}} \times 100 \tag{4}$$

$$Y_{DME} = \frac{2Py_{DME}}{F(y_{CO})_{in}} \times 100 \tag{5}$$

where F and P are the molar flow rates of feed and product (mol/h) and y_i is the mole fraction of component i in the feed stream $(y_i)_{in}$ or in the product stream $(y_i)_{out}$.

The selectivity of DME in carbon products ($S_{DME\ CP}$) is calculated as the ratio of carbon in the DME to the sum of carbon contents corresponding to all carbon containing products at outlet stream [6]:

$$S_{DME\ CP} = \frac{2y_{DME}}{2y_{DME} + y_{CH_3OH} + y_{CO_2} + y_{CH_4} + 3y_{C_3H_8}} \tag{6}$$

3. Results and discussion

3.1. Textural and acidic properties of catalysts

Table 1 shows the physical properties of the metallic function, the acidic function and of the bi-functional catalyst. It is observed that the bi-functional catalyst has lower surface area than acid function and methanol synthesis catalyst which can be tentatively assigned to filling of parts of the methanol synthesis catalyst pores with zeolite.

XRD spectra of the metallic function, the acidic function and of the hybrid catalyst are shown in Fig. 2. In the metallic function (CuO–ZnO–Al_2O_3 catalyst), there are peaks that can be ascribed to CuO crystal phases and Al_2O_3 crystal phases based on JCPDS file no. 041-0254 and 04-0879, respectively. There are no peaks of ZnO, suggesting that the ZnO is highly

Table 1
Properties of the individual functions and of the bi-functional catalyst (metallic to acidic function = 3:1)

Catalyst	BET surface area ($m^2\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)	Total pore volume ($m^3\ g^{-1}$)	Micropore volume ($m^3\ g^{-1}$)	Average pore radius (Å)
CuO–ZnO–Al_2O_3	84	0.369	0.327	0.00018	77.8
H-MFI-90	392	72.44	0.389	0.0359	19.9
CuO–ZnO–Al_2O_3/H-MFI-90	33	90.96	0.191	0.0932	28.7

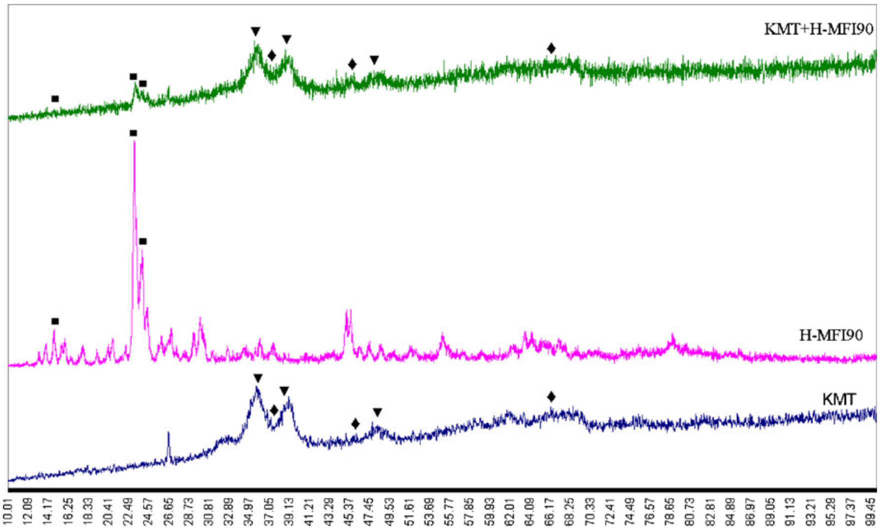

Fig. 2. XRD patterns of solid acid catalyst (H-MFI90), methanol synthesis catalyst (KMT) and bi-functional catalyst (KMT + H-MFI90) [(▼) CuO; (♦) Al_2O_3; (■) $(Al_2O_3)_{1.5}(SiO_2)_{0.072}$].

dispersed in the catalyst. In the XRD spectrum of H-MFI-90, aluminum silicon oxide ($(Al_2O_3)_{1.5}(SiO_2)_{0.072}$) crystal phases, based on JCPDS file no.42-0305 can be seen. In the bi-functional catalyst, all peaks of the XRD patterns become weaker and wider due to more dispersion of crystal phases.

Fig. 3 shows the H_2-TPR patterns of methanol synthesis catalyst and of bi-functional catalyst (BFC). One reduction peak at the temperature range 125–250 °C can be observed for the two catalysts, which can be attributed to the reduction of CuO. By comparing the profiles of methanol synthesis catalyst with BFC, it is clear that the reducible CuO peak appears at 197 °C on the methanol synthesis catalyst, while it appears at 232 °C on the BFC which showed that 250 °C is a suitable reduction temperature that was used for BFC. It means that the addition of an acidic function (H-MFI-90) to a metallic function ($CuO–ZnO–Al_2O_3$) made CuO more difficult to be reduced. It other words, it may imply that physically mixing the methanol synthesis component with H-MFI-90, restricts the reducibility of CuO crystal phases.

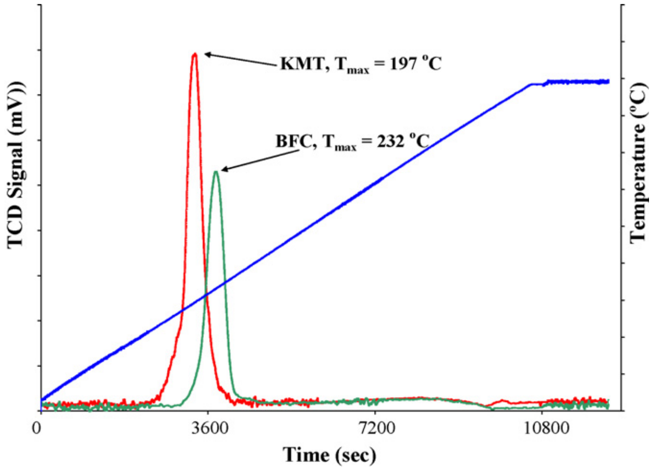

Fig. 3. H_2-TPR profiles of the methanol synthesis catalyst (KMT) and bi-functional catalyst.

NH_3-TPD was performed to monitor the acid strength and the amounts of acid sites on the H-MFI-90. As shown in Fig. 4, two major NH_3 desorption peaks as well as a shoulder peak can be observed at 222 °C (weak acid sites) and 450 °C (strong acid sites) and 685 °C, respectively. The amount of NH_3 desorption based on the area under the first peak is 9.39×10^{-2} cm^3 (NH_3)/g-cat, from second peak is 5.21×10^{-2} cm^3 (NH_3)/g-cat and for shoulder peak is 8.76×10^{-3} cm^3 (NH_3)/g-cat. Thus, the total acid sites density is 0.1 cm^3 (NH_3)/g-cat [3]. So it can be said that this type of zeolite has not any acid sites with medium strength. The weak acid sites are related to the external surface or to some type of extraneous material or interaction of ammonia molecules with surface oxide or hydroxyl groups by non-specific hydrogen bonding [3]. Quantitative analysis of the two parts of bi-functional catalyst that was obtained by XRF results has been shown in Table 2. The major components of methanol synthesis catalyst are CuO (52.1 wt.%), ZnO (26.2 wt.%), equal to atomic ratio of Cu/Zn = 2 and Al_2O_3 (4.4 wt.%) and for methanol dehydration catalyst are SiO_2 (93.27 wt.%) and Al_2O_3 (1.46 wt.%) or molar ratio of $SiO_2/Al_2O_3 = 90$.

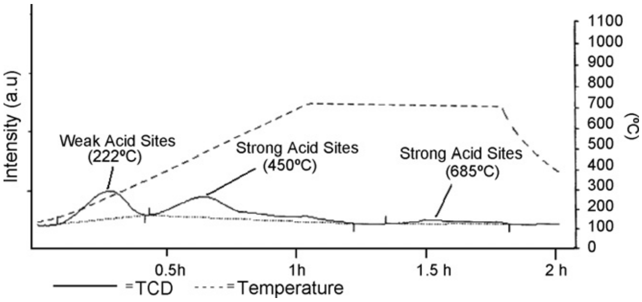

Fig. 4. TPD spectrum of H-MFI90 zeolite as dehydration component in the bi-functional catalyst.

Table 2
Chemical composition (wt.%) of the metallic and acidic function of the bi-functional catalyst

Components	Methanol synthesis catalyst	Methanol dehydration catalyst
CuO	52.1	0.004
ZnO	26.2	0.005
Al_2O_3	4.40	1.46
SiO_2	0.46	93.27
Others	16.84	5.261

3.2. *Long-term activity and stability tests*

In order to investigate the simultaneous effect of temperature and feed composition on the catalytic performance of bi-functional catalyst over 60 h time on stream, the general full factorial design method with two factors including temperature in three levels 200, 220, 240 °C and H_2/CO molar ratio of feed in three levels 1, 1.5, 2 and 3 replicates for each treatment was applied (Table 3) [7,8].

In the figures corresponding to experimental results, except for time on stream plots, the data points are the average ones and error bars with 95% confidence ($\alpha = 0.05$) interval have been drawn.

The other operating conditions which was maintained constant during all stability tests have the following values: pressure, 35 bar; catalyst loading, 10.5 g bi-functional catalyst in 350 g solvent; impeller speed, 1600 rpm; space velocity, 1100 mLn/(g-cat h); molar feed rate, 0.472 mol of ($H_2 + CO + N_2$)/h. The selection of 1600 rpm for impeller speed and 1100 mLn/(g-cat h) for space velocity is based on the experimental results from independent tests under which there are no mass transfer restrictions and the reaction system is far from the thermodynamic equilibrium region. Equilibrium state established in this system at the space velocity less than 500 mLn/(g-cat h) where with decreasing space velocity syn gas conversion remain unchanged. CO conversion (X_{CO}), yield of DME (Y_{DME}) and selectivity of DME (S_{DME}) have been used for comparing the performance of the hybrid catalyst under different operational conditions.

3.2.1. *Effect of temperature and feed composition*

The changes in the X_{CO}, Y_{DME} and S_{DME} as a function of reaction time for $H_2/CO = 1$, $P = 35$ bar and space velocity = 1100 mLn/(g-cat h) are shown in Figs. 5–7. For the other conditions the same trend can be seen.

It is obvious from the figures that, this bi-functional catalytic system showed good activity and stability for the all operating conditions. For each run, there is an initial period for which the X_{CO} or Y_{DME} increases until a certain level is reached and, thereafter starts to decrease slowly or remains approximately constant at those certain levels within ±3 variation. Erena et al. [6] reported that this initial period is a characteristic of the metallic functions used for syn gas and CO_2 transformation. During this period catalyst equilibration occurs as a consequence of the oxidation–reduction of metallic active sites. In this period, catalyst activity increases until a stable condition is reached and,

Table 3
Specifications of nine activity and stability tests at the CuO–ZnO–Al_2O_3:HMFI-90 = 3:1 wt.%, $P = 35$ bar, SV = 1100 mLn/(g-cat h)

Run no.	Temperature (°C)	H_2/CO ratio
1	220	1
2	240	1
3	260	1
4	220	1.5
5	240	1.5
6	260	1.5
7	220	2
8	240	2
9	260	2

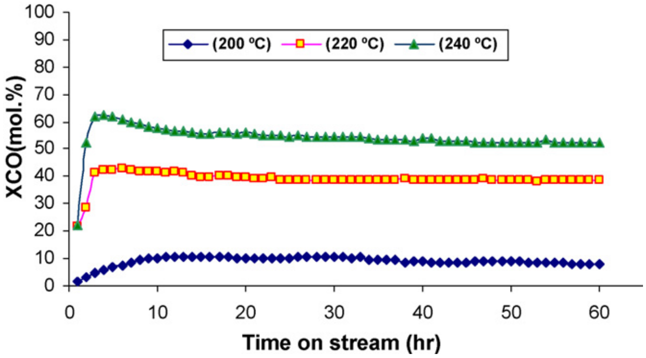

Fig. 5. Variation of CO conversion (X_{CO}) as a function of time on stream for different temperatures at $H_2/CO = 1$, $P = 35$ bar, SV = 1100 mLn/(g-cat h).

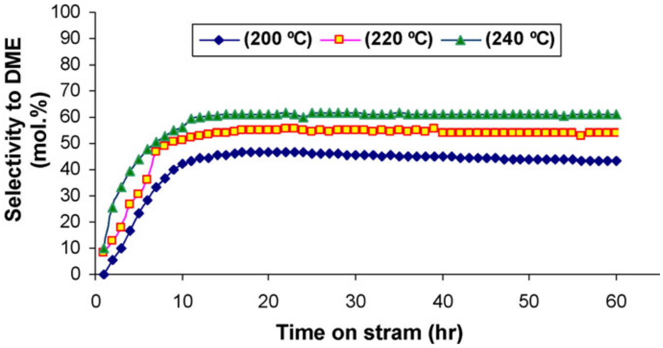

Fig. 6. Selectivity of DME (S_{DME}) vs. time on stream for different temperatures, at $H_2/CO = 1$, $P = 35$ bar, SV = 1100 mLn/(g-cat h).

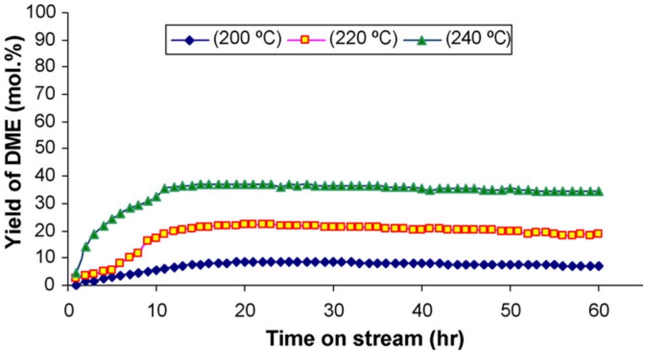

Fig. 7. Yield of DME (Y_{DME}) vs. time on stream for different temperatures at $H_2/CO = 1$, $P = 35$ bar, SV = 1100 mLn/(g-cat h).

Table 4
Effect of operating conditions on catalytic performance of $CuO–ZnO–Al_2O_3$/HMFI-90 ($CuO–ZnO–Al_2O_3$:HMFI-90 = 3:1 wt.%, $P = 35$ bar, SV = 1100 mLn/(g-cat h)

T (°C)	H_2/CO	X_{CO} (mol%)	DME yield (mol%)	Selectivity (C-mol%)			
				DME	CO_2	Hydrocarbons ($CH_4 + C_3H_8$)	MeOH
200	1	9.0	8.5	48.8	16.2	0.4	34.7
220	1	39.1	18.7	50.4	27.5	0.9	21.2
240	1	54.2	33.8	61.5	28.6	1.9	8.7
200	1.5	11.6	11.3	36.3	18.6	0.7	44.5
220	1.5	44.2	22.0	45.3	19.3	1.1	34.2
240	1.5	68.5	40.8	61.9	27.7	1.7	8.7
200	2	25.9	14.4	41.8	27.0	1.6	29.6
220	2	53.9	27.6	51.0	30.5	2.6	15.9
240	2	79.6	47.1	61.1	29.4	2.8	6.7

subsequently, the behavior of the catalyst is only altered by slow deactivation. Table 4 shows performance of this hybrid catalyst under different operating conditions. As can be seen from this table, with increasing temperature and H_2 to CO molar ratio in the feed, X_{CO}, S_{DME} and Y_{DME} also increase, which can be attributed to better synergetic effect of the reaction system at those conditions. Almost similar results are also reported previously by other researchers [9,10]. Carbon dioxide is also formed in large quantities especially at $T = 240$ °C since the WGS reaction, which is parallel to MeOH synthesis reaction [Eqs. (1) and (3)], is kinetically enhanced by an increase in the reaction temperature [9]. Methanation plays almost no role in all cases; since the experimental conditions adopted here are rather moderate [9], however it should be noted that higher temperatures and H_2/CO molar ratios favor side reactions which consist primarily of the further conversion of DME to lower olefins and their subsequent hydrogenation (saturation) to the corresponding paraffins (the concentration of CH_4 has increased from 0 at 200 °C and $H_2/CO = 1$ to 0.321 mol% at 240 °C and $H_2/CO = 2$) [9]. The general reaction scheme given by Chang and Silvestri can be outlined as follows [11]:

$$2CH_3OH \xrightarrow{-H_2O} CH_3OCH_3 \xrightarrow{-H_2O} C_2\text{–}C_5 \text{ Olefins} \qquad (7)$$

Nevertheless, the very low concentration of methane and propane even at $H_2/CO = 2$ and the absence of any heavier hydrocarbons in the product stream reveals moderate acidity of H-MFI-90 zeolite (476 μmol/g-cat, $SiO_2/Al_2O_3 = 90$ mol/mol) that inhibits deep dehydration of methanol to light olefins which finally causes coke deposition and deactivation of bi-functional catalyst.

From the activity point of view, with increase in the temperature and H_2 content of feed, X_{CO}, Y_{DME} and S_{DME} increased. Maximum values of these parameters are $X_{CO} = 79.62\%$, $Y_{DME} = 47.05\%$ and $S_{DME} = 59.96\%$, that was obtained at $T = 240$ °C and $H_2/CO = 2$. In fact, as long as a reaction system is far from the thermodynamic equilibrium region, from a kinetics point of view, increasing the temperature can lead to the higher reaction rates and consequently, higher consumption rates of limiting reactant (carbon monoxide in our case). For example, conversion of CO for $H_2/CO = 1$, increases from 9% to 53.8% (molar basis) with increasing the temperature from 220 to 260 °C. Erena et al. [6] reported 275 °C as the optimum temperature for direct synthesis of DME in a plug-flow gas phase reactor over a $CuO–ZnO–Al_2O_3$/NaHZSM-5 bi-functional catalyst. Mao et al. [3] reported 260 °C as the optimum reaction temperature in a tabular reactor for direct DME synthesis over CuZnAlMn catalyst. Anyway the optimum temperature for direct synthesis of DME must lie between 230–280 °C [6,9], which is a compromise between higher activity (CO conversion) and lower DME selectivity (higher selectivity for CO_2, methane and other low hydrocarbons) with increasing temperature.

The main effect and interaction plots are used for interpreting of experimental results. As can be seen from Table 4, under a specified temperature and pressure, X_{CO} increases with the increase of H_2 to CO molar ratio. The synergy shows that, with the increase of H_2/CO ratio, methanol synthesis reaction is accelerated, which leads to higher CO conversion [12]. Not surprisingly, the conversion of CO is greater than that of H_2 over the whole range of operating conditions. This is due to water gas shift reaction [13] which produces H_2 in the reaction medium and this finally leads to decrease the total conversion of H_2. At the same time, similar to X_{CO}, Y_{DME} also increases with the increase of H_2 content (Table 4), which can be attributed to high catalytic activity of both methanol synthesis and methanol dehydration components of bi-functional catalyst even at high H_2/CO ratios. The increase of H_2/CO ratio suppresses water gas shift reaction which consumes H_2O. Since, H_2O is the product of methanol dehydration reaction, the increase of H_2/CO ratio results in the accumulation of H_2O and poor chemical synergy [14]. But this is not the case for our catalytic system, because for $H_2/CO = 2$ there was only small amounts of H_2O in the product stream (=1.9%) and besides, there is slight difference between the evolution of CO_2 productivity over time on stream and that of DME (Fig. 8) which reveals high catalytic activity of methanol synthesis function of bi-functional catalyst, specially for water gas shift reaction, that effectively consumes the H_2O product of methanol dehydration reaction and generates CO_2. This explanation especially is more clear for initial TOS that the active centers of the bi-functional catalyst are almost fresh and have high tendency for adsorbing the H_2O molecules. In fact at the same operating conditions, the rate of the water gas shift reaction is much greater than the rate of the other two reactions [14]. This is easily confirmed by com-

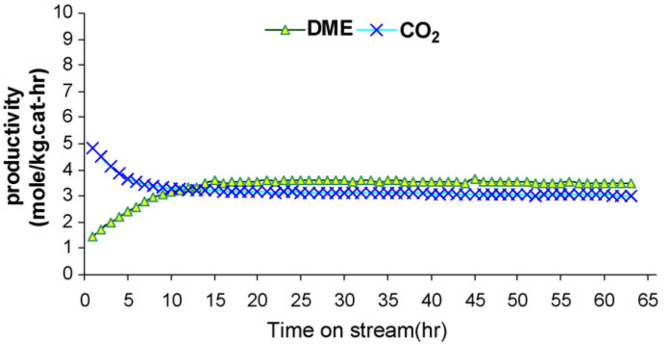

Fig. 8. Evolution of DME and CO_2 productivity at $H_2/CO = 2$, $P = 35$ bar, $T = 240\,^{\circ}C$, SV = 1100 mLn/(g-cat h).

paring Gibbs free energy changes for these three reactions. The optimum ratio of $H_2/CO = 2$, has also been obtained by Erena et al. [6]. In the case of Y_{DME} or S_{DME}, with the increasing temperature, these two parameters keep increasing, because high temperature is more favorable for the performance of MeOH dehydration catalyst rather than MeOH synthesis catalyst [12]. In the other words, MeOH synthesis catalyst is more active at lower temperatures compared with MeOH dehydration catalyst that is more active at higher temperatures [13]. This is more clear for CO rich syn gas. For example, at $H_2/CO = 2$ and based on the plots for time averaged values of Y_{DME} over 60 h time on stream as a function of temperature, increasing the temperature from 220 to 260 °C have led to 75.22% increase in Y_{DME} whereas for $H_2/CO = 1$ is 78.94% (molar basis) which can be attributed to higher synergetic effect for the greater proportion of CO in the feed [14,15,16].

3.3. Analysis of experimental data

Factorial designs allow for the simultaneous study of the effects that several factors may have on a process. In a general full factorial experiment in which at least one factor has more than two levels, responses are measured at all combinations of the experimental factor levels. However, it should be noted that the general full factorial design method is used when the number of factors and their associated levels is small. As pointed out in previous sections, from the number of factors, levels and replicates that have been selected for creating a general full factorial experiment; we performed 27 runs which were essentially consisted of nine major experiments with three replicates for each of them. After gathering the experimental data, the general linear model procedure was used to conduct an analysis of variance (ANOVA) to determine which of the factor will affect the catalytic performance significantly [7,8].

Table 5
Factor table

Factor	Type	Levels	Values
T (°C)	Fixed	3	200, 220, 240
H_2/CO	Fixed	3	1, 1.5, 2

To do this, the yield of DME as response with temperature and H_2/CO molar ratios of feed have been chosen as fixed factors. The relative percentage contribution among the factors is determined by comparing their relative variance. The ANOVA will compute the quantities such as degrees of freedom (d.f.), sequential sums of squares (Seq SS), adjusted sums of squares (Adj SS), variance (V), F-ratio, p-value (P) and relative percentage contribution. For fixed factors, the ANOVA examines whether the factor level means are the same or different. The results are shown in Tables 5 and 6. The most important statistic in the analysis of variance table is the p-value (P). As can be seen from Table 6 there is a p-value for each term in the model (except for the error term). The p-value for a term tells us whether the effect for that term is significant or not. In other words, if P is less than or equal to the α-level we have selected, then the effect for the term is significant. In the ANOVA table (Table 6), the effect of temperature, H_2/CO molar ratio of feed and the temperature by H_2/CO molar ratio of feed interaction are assessed. Remembering that α-level is 0.05, the results indicate that: (1) the p-value for the temperature factor is given as 0.000. This means that the actual p-value is less than 0.0005. Since this is less than the chosen α-level of 0.05, it means the effect of temperature on the yield of DME is significant. In other words, the mean yield of DME is different for the different temperature levels (Table 6). (2) The p-value for feed composition is also less than 0.05, indicating that there is also a significant effect of H_2/CO on yield. In the other words, the mean yield of DME is different for the different feed compositions (Table 7). (3) The p-value for the interaction term is also less than 0.05. Thus, the interaction of the temperature and feed composition has also significant effect on the yield of DME. In other words, the effects of temperature on the yield of DME are different at different levels of feed compositions. The last column of the ANOVA table indicates the relative percent contribution of each factor. The results in the table show that temperature of process contributes the most which is 90.61%. The contribution of feed composition and the interaction of temperature by feed composition is 8.18

Table 6
ANOVA table

Source	d.f.	Seq SS	Adj SS	Variance	F	P	Percentage contribution (%)
Temperature (°C)	2	4898.05	4898.05	2449.02	110.000	0.000	90.61
H_2/CO of feed	2	441.97	441.97	220.98	9981.91	0.000	8.18
Temperature (°C) × H_2/CO	4	65.14	65.14	16.29	735.65	0.000	1.2
Error	18	0.40	0.40	0.02			
Total	26	5405.56					100

Table 7
Least squares means for yield of DME

Temperature (°C)	Mean	Standard error of mean
200	11.475	0.04960
220	26.457	0.04960
240	44.422	0.04960

H_2/CO of feed	Mean	Standard error of mean
1	22.346	0.04960
1.5	27.767	0.04960
2	32.241	0.04960

Interaction	Mean	Standard error of mean
200 × 1.0	8.554	0.08590
200 × 1.5	11.475	0.08590
200 × 2.0	14.397	0.08590
220 × 1.0	21.953	0.08590
220 × 1.5	26.457	0.08590
220 × 2.0	30.960	0.08590
240 × 1.0	36.530	0.08590
240 × 1.5	45.370	0.08590
240 × 2.0	51.367	0.08590

and 1.2%, respectively. The small relative percentage contribution of interaction term as compared to two other terms indicates that the effect of this term on the response variable is not as large as of the effect of temperature and H_2/CO molar ratio of feed.

In order to confirm the results of ANOVA table, we can use a main effect and an interaction plot. A main effect plot is used to determine which factors influence the response and to compare the relative strength of the effects. An interaction plot, in other words, is to determine if two factors interact in their effect on the response. These plots are shown in Figs. 9 and 10, respectively. Each data point in the Fig. 9 represents the mean of response variable (yield of DME) for each factor level. Also, the dotted red line represents a reference line at the overall mean, which is approx. 27.34. The plots indicate that both temperature and H_2/CO molar ratio of feed have positive effect on yield of DME. In other words, with the increase of temperature and H_2 content of feed in the specified region, yield of DME increases. By comparing the slopes of the lines, we can compare the relative magnitude of the factor effects. Thus it is clear that the temperature has greater effect on the bi-functional catalyst activity as compared to the feed composition. This result is consistent with the p-value and the relative percentage contribution of temperature and H_2/CO molar ratio of feed in the ANOVA table.

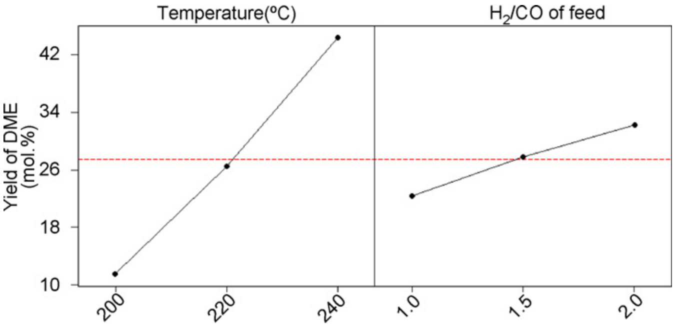

Fig. 9. Main effect plot (data means) for yield of DME.

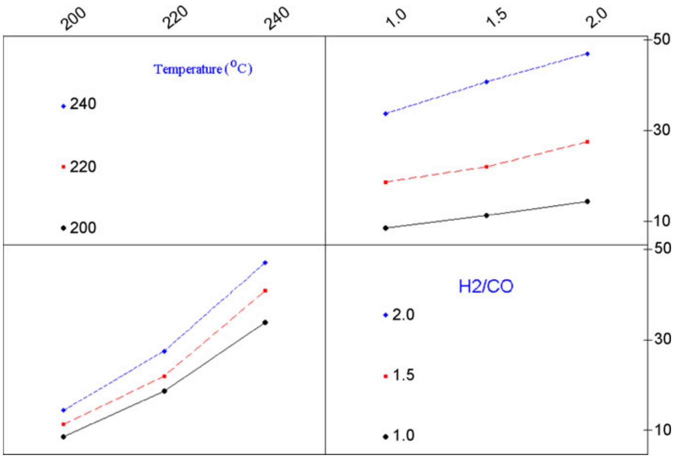

Fig. 10. Interaction plot (data means) for yield of DME.

As we know an interaction is present when the change in the response mean from the low to the high level of a factor depends on the level of a second factor. It is clear from Fig. 10 that there is no noticeable interaction between temperature and feed composition because the lines are approximately parallel, except in the 220–240 °C (in the lower left corner) limit in which the slopes of lines for H_2/CO equal to 1, 1.5 and 2 suggest a poor interaction. Also this result is consistent with the results of ANOVA table, in which the interaction term has small relative percentage contribution on response variable.

4. Conclusion

Activity and durability of a bi-functional catalyst made up of a metallic function (CuO–ZnO–Al_2O_3) and an acidic function (H-MFI90 zeolite) has been studied by factorial experimental design method for direct syn gas transformation into DME in a mechanically agitated slurry reactor system. The almost identical time on stream plots for yield of DME (Y_{DME}) under the whole operating conditions proved that the catalyst had good stability. One of the salient features of these plots was the existence of an initial period for which catalyst equilibration occurs as a consequence of successive oxidation–reduction of metallic active sites. The outstanding catalytic performance is owing to the suitable matching of the metallic and acidic functions of bi-functional catalyst for both CO hydrogenation step (from CO to methanol) and dehydration step (from methanol to DME) that leads to strong synergetic effect of the reaction system. Furthermore, the moderate acid strength of dehydration component (H-MFI90) is a key factor that minimizes side reactions of transformation of MeOH and DME into hydrocarbons which eventually deposit on catalyst as coke and deactivate it. From the results of Table 4 and based on the kinetics aspects, it seems that the effect of temperature can outweigh the influence of H_2/CO molar ratio in the studied range on the activity of the catalyst. This was confirmed by the results of ANOVA table and main effect plot for yield of DME. This systematic method of investigation of the effects of operating conditions showed that for our bi-functional catalytic system at the fixed space velocity (1100 mLn/(g-cat h)) and pressure (35 bar), temperature of 240 °C and molar ratio of H_2/CO in the feed equal to 2 are the optimal operating conditions for having maximum yield of DME.

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