

Bifunctional Catalysts Synthesis and Determination of Kinetic Parameters for Direct Conversion of Syn Gas to Di-methyl Ether

Ali Hadipourⁱ; Morteza Sohrabiⁱⁱ

ABSTRACT

In the present study, the catalyst preparation and reaction kinetic modeling of syngas transformation into dimethyl ether using a mixture of metallic oxides, (CuO, ZnO, Al₂O₃) and an acidic component (γ -Al₂O₃) as catalyst has been investigated. Twenty three catalysts were prepared according to a pre-designed research program consisting of four phases. In each phase, applying the Taguchi experimental design method, a number of catalysts was synthesized by co-precipitation method, using different percent of metal nitrates solutions. It was noted that the ZnO content of the catalyst, the nature of the precipitant agent, mass ratio of gamma-alumina to total metal oxides and calcination temperature, had the highest impacts on the activity of the catalysts.

Catalysts activity and kinetic measurements were carried out using a catalytic fixed bed micro reactor. The operating temperature range was 230-300 °C and the pressure was 8 barg. The experimental runs were performed applying a wide range of catalyst to feed ratios. A kinetic expression devised, based on Graff model for methanol synthesis and Bercic model for methanol dehydration and was correlated with the experimental results obtained in this study. The degree of agreement between the two sets of data was 90-95%.

KEYWORDS

DME, bifunctional catalysts, activity measurement, kinetic parameter

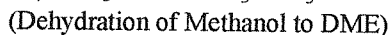
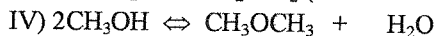
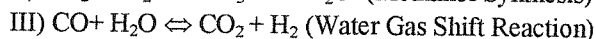
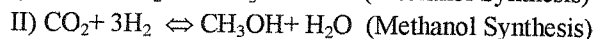
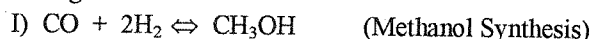
1. INTRODUCTION

Dimethyl ether (DME) is an intermediate in the preparation of a number of industrial chemicals. It has also found an increasing application in aerosol industry as an ozone friendly propellant. DME vapor pressure is 6.1 bara (25 °C), hence can be stored and transported easily (like LPG) in comparison with other fuels. In addition, it has higher cetane number than diesel fuel (60 v.s. 50) and no sulfur content, hence can be used as an ultra-clean fuel (low No_x, near zero smoke, less engine noise) for diesel engines [1]-[3].

Commercial production of dimethyl ether is achieved using either of the following two methods, 1) a two-step procedure consisting of methanol formation from synthesis gas followed by the dehydration of the latter and 2) a single step process, that is the direct formation of DME from synthesis gas. In comparison with the two-step

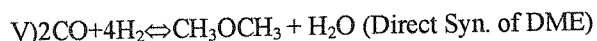
method, the single-step procedure is attracting more attention for its dramatic economic value and theoretical significance [4].

A bifunctional catalyst for conversion of synthesis gas to DME normally contains two types of active sites used for methanol formation and methanol dehydration, respectively. These catalysts usually contain zinc, copper and aluminum oxides (for methanol formation) and gamma-alumina as a zeolite (for methanol dehydration) and are prepared by the co-precipitation method [5]-[10]. For further information refer to ref.[11]. DME can be obtained directly from synthesis gas according to the following reactions:



ⁱ A.Hadipour is with the Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran (e-mail: hadipour_a@yahoo.com).

ⁱⁱ M.Sohrabi is with the Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran (e-mail: sohrabi@aut.ac.ir).



In the present study, synthesis and activity measurement of some DME catalysts were performed within a program consisted of four phases. In the first phase, according to Taguchi experimental design method [12], sixteen catalyst's samples were prepared and tested. In the second phase, taking into account the results obtained from the previous phase, two samples were synthesized. In the third phase, two samples and finally, in the last phase three more samples were prepared and tested. The particular catalyst, having the highest activity was noted and the constituents of the latter were presented.

Finally, the reaction kinetic parameters that have been determined for DME synthesis from syngas has been developed and correlated with experimental results.

2. EXPERIMENTAL

A. Material

The chemicals used in the present study were all analytical grades and supplied by Merck and BASF, Germany. These were copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, aluminum nitrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, sodium carbonate $[\text{Na}_2\text{CO}_3]$, ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ and γ -alumina (acidity 20%, porosity 0.7 ml/g and cylindrical form with id=4 mm). The purity of the gases used was 99.999 percent.

B. Catalyst preparation

A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and a solution of Na_2CO_3 were co-precipitated when added simultaneously and drop wise to a beaker containing deionized water over a period of 30 min at 70°C , under continuous stirring. The precipitates formed were aged for an additional hour under continuous stirring at 70°C . The precipitate were then filtered and washed several times with deionized water to remove residual sodium ions, and added to a suspended liquid having dehydration component (γ -alumina) and water. The final suspension was aged under stirring at 70°C for 1 hour. The precipitate was then filtered and the solid obtained was dried at 120°C for 8 hours and calcined in flowing air for 5 hours (the catalyst was slowly heated up to calcination temperature (60°C/hr) and after 5 hours at this temperature, the catalyst was ready for operation.). The BET surface area of the catalyst was measured using a Quantasorb apparatus (from Quantachrome Company). The XRF and XRD patterns of catalysts were also determined.

C. Activity measurement

Catalytic activity of all samples in converting synthesis gas to DME were studied under unsteady state conditions in a fixed bed flow reactor (i.d. 6.4mm and length 650 mm) connected on line to a GC apparatus. The catalyst was packed in a stainless steel tube equipped with a

thermocouple placed in the catalyst bed. Experiments were performed in temperatures ranging from $230\text{--}300^\circ\text{C}$ and a constant pressure of 8 barg. Prior to catalytic testing, the samples were crushed and sieved to fine powders (grain size equal to $100\text{--}150\ \mu\text{m}$). In each experimental run, about 1-2 grams of catalyst was loaded in the reactor having two stainless steel supports at both ends of the catalyst bed. A schematic diagram of the experimental rig is shown in Figure 1. The reactor system was first purged with nitrogen gas and then pressurized. The catalysts were reduced in a flowing hydrogen gas diluted with nitrogen. The temperature was raised to 150°C (100°C/hr) under flow of nitrogen. At this temperature, hydrogen was added to the nitrogen stream to the level of 50% and the temperature was further raised to 200°C (at a rate of 25°C/hr). Finally, the hydrogen concentration was increased to 100 % and the temperature raised to that of the reaction ($230\text{--}300^\circ\text{C}$). The catalyst was remained at this temperature for 4 hours before being applied in the reaction.

A mixture of 4 vol. % CO_2 , 32 vol. % CO and 64 vol. % H_2 entered the top section of the reactor that acted as a pre-heater ($25\text{--}300^\circ\text{C}$). Three mass flow meters (Brooks, Model 5850) and a control system were used to monitor the individual gas flow rates and to provide the required gas mixtures.

A portion of the effluent gas, after reducing its pressure by a back pressure regulator, was directed to a gas chromatograph apparatus (Agilent- 6890) connected on - line to the system. The effluent gas was analyzed several times with four to seven minutes intervals during each experimental run. The GC column was packed with Porapak Q with 80–100 mesh. The column temperature was increased steadily from 70 to 200°C and remained at that level for 4 minutes. Helium was used as a carrier gas with a flow rate of $2.5\ \text{cm}^3/\text{min}$. The thermal conductivity detector was applied.

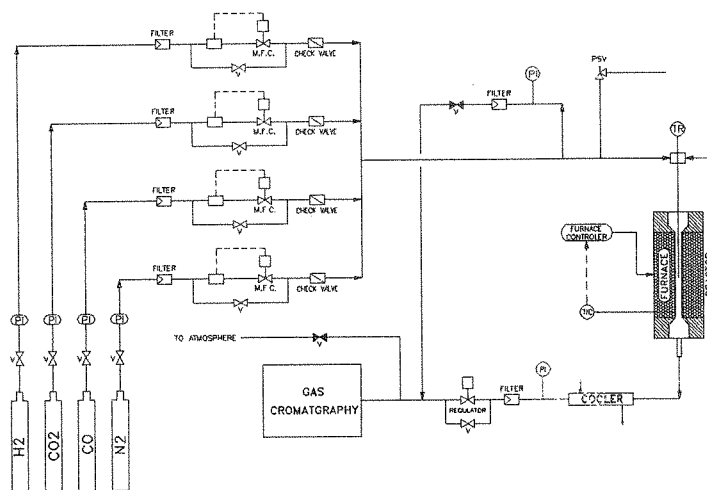


Figure 1: Schematic diagram of the reactor setup.

3. RESULTS AND DISCUSSION

A. Catalyst preparation

To apply the Taguchi method to the initial preparation phase, the pertinent parameters of the catalyst synthesis were selected as follows:

- (X) concentration of copper oxide
- (Y) concentration of zinc oxide
- (Z) concentration of aluminum oxide

Four levels were considered for each parameter. An appropriate arrangement for the present system was, therefore, an L-16 configuration [12]. Arrangements of the parameters and the related levels are shown in Table 1.

Sixteen samples (CDME-1–CDME-16) were prepared and accordingly, sixteen experimental programs were performed, from which, the optimum conditions were determined. In the above runs; the final activity of catalysts has been taken as the response of the system. In Figure 2, the vertical bar type presentation of the average response of the system to various levels of parameters are demonstrated.

The above results reveal the presence of certain interactions between the parameters. To determine the extent of such interactions, the response of each parameter in connection with the rest of them was considered. The results of analysis are presented in Table 2. The latter indicates some extensive interactions between X-Y and X-Z parameters. This is due to the DME synthesis from CO hydrogenation at the copper surface of catalyst [9].

Basically, a larger response corresponds to the better catalysts characteristic. However, the relative importance among the catalyst preparation parameters for the performance characteristic still needs to be known, so that the optimal combinations of the catalyst preparation parameters level can be determined more accurately. By considering the above observation the optimum conditions for the catalyst synthesis were determined as X4, Y1 and Z4 (CDME-13). In other words, the optimum parameters for the present catalyst may be summarized as follows:

- Concentration of copper nitrate: 31.96 (VoL. %)
- Concentration of zinc nitrate: 9.76 (VoL. %)
- Concentration of aluminum nitrate: 39.69 (VoL. %)

Analysis of the data (ANOVA table) as given in Figure 3, indicates that the relative impact of three parameter upon the final activity of catalyst is as $ZnO > CuO > Al_2O_3$. In addition, the F-test [13] can also be used to determine which catalyst preparation parameters have a significant effect on the performance characteristic. From the Fisher tables [13] with 95% confidence, $F_{0.05, 3, 6}$ was found to be 4.76. The F values for X, Y and Z obtained from Taguchi method were 16.80, 66.85 and 6.52, respectively. These are greater than the corresponding values in Fisher tables. The tests are, therefore, reliable with 95% confidence. It seems that these parameters have great impact on the performance characteristic of the catalyst prepared. The calculation error was 5.426%.

Referring to Figure 2, it may be observed that excess of ZnO in catalysts has a negative effect on the activity, while presence of CuO and Al_2O_3 enhances the catalyst activity. These finding could be explained by noting that presence of copper and aluminum oxides increases the dispersion of active sites and hence promotes the surface area of catalyst, while ZnO has a reverse effect on catalyst activity. These observations may be confirmed by comparing the surface area and other data for samples CDME-1 and CDME-4, CDME-5 and CDME-8, CDME-9 and CDME-12, CDME-13 and CDME-16, as presented in Table 3.

In the second phase, the effect of precipitant nature (sodium carbonate and ammonium carbonate) on the catalysts activity was studied. Two more samples (CDME-17 – CDME-18) were prepared and tested. It was found that the activities of catalysts using ammonium carbonate as a precipitating agent were normally higher than those applying sodium carbonate. This could be due to the non-desirable effect of sodium on the catalysts activity. The Na^+ ions could reduce the number of acid sites of dehydration component (γ -alumina) of the catalyst [14], and subsequently, reduce the activity of the catalyst (methanol undergoes dehydration to form DME over solid acid sites of the catalyst).

In the third phase, the influence of the acidic component (γ -alumina) of the catalysts on the activity of the latter was considered. Two more samples (CDME-19 – CDME-20) were synthesized and tested. It was observed that the highest activity was obtained at the weight ratio of 1:1 of the total metal oxide to γ -alumina (CDME-18 – CDME-20). This may be due to the adequate and uniform dispersion of γ -alumina within the metal oxides phase.

Finally, in the fourth phase, the effect of calcination temperature on the catalysts activity was investigated. Accordingly, three more samples (CDME-21 – CDME-23) were prepared and tested. It was found that the highest activity was obtained in case of 350 °C calcination temperature (CDME-18, CDME-21 – CDME-23). This may be explained by assuming that at higher calcination temperatures partial sintering of catalysts particles could be occurred and the active area of catalyst is reduced, Sohrabi *et al.* [15] have reported a similar observation, stating that with an increase in calcinations temperature the copper crystallite particle size increases and acts as backbones of water gas shift reaction.

Based on XRF results, the weight percent of the constituents of the optimum catalyst were 53.1 Al_2O_3 , 34.7 CuO and 9.4 ZnO .

In Table 3, some further properties of some catalysts are given (activities were determined at 250 °C and 8 barg). cCatalyst's activities were measured as mg of DME formed per hour per gram of catalyst. These are presented in Table 4.

TABLE 1
ARRANGEMENT OF PARAMETERS IN L-16 PRESENTATION

Catalyst number	X	Y	Z
CDME-1	1	1	1
CDME-2	1	2	2
CDME-3	1	3	3
CDME-4	1	4	4
CDME-5	2	1	2
CDME-6	2	2	1
CDME-7	2	3	4
CDME-8	2	4	3
CDME-9	3	1	3
CDME-10	3	2	4
CDME-11	3	3	1
CDME-12	3	4	2
CDME-13	4	1	4
CDME-14	4	2	3
CDME-15	4	3	2
CDME-16	4	4	1

TABLE 2

RESULTS OF PERCENT OF INTERACTION BETWEEN THE CATALYST PREPARATION PARAMETERS

Preparation parameter	X	Y	Z
X	-	10.92	38.89
Y	10.92	-	19.33
Z	38.89	19.33	-

TABLE 3

CERTAIN PROPERTIES AND ACTIVITIES OF SOME DME SYNTHESIS CATALYSTS

Catalyst name	Calcination temp. (°C)	Total area (BET) (m ² /g cat)	Major cryst. phases	*Activity (mg DME)/(g cat..h)
CDME-1	350	143.24	CuO, ZnO, Al ₂ O ₃	6.26
CDME-4	350	121.14	CuO, ZnO, Al ₂ O ₃	2.79
CDME-5	350	146.76	CuO, ZnO, Al ₂ O ₃	9.31
CDME-8	350	124.39	CuO, ZnO, Al ₂ O ₃	3.21
CDME-9	350	240.32	CuO, ZnO, Al ₂ O ₃	12.87
CDME-12	350	150.72	CuO, ZnO, Al ₂ O ₃	3.63
CDME-13	350	251.32	CuO, ZnO, Al ₂ O ₃	12.87
CDME-16	350	130.25	CuO, ZnO, Al ₂ O ₃	3.88
CDME-18	350	257.46	CuO, ZnO, Al ₂ O ₃	14.27
CDME-22	500	-	CuO, ZnO, Al ₂ O ₃	3.76
CDME-23	700	65.25	CuO, ZnO, Al ₂ O ₃	2.45

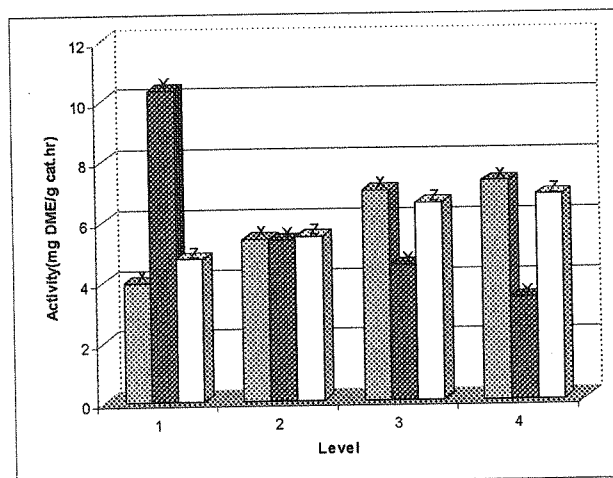


Figure 2: Average system response to parameters at various levels.

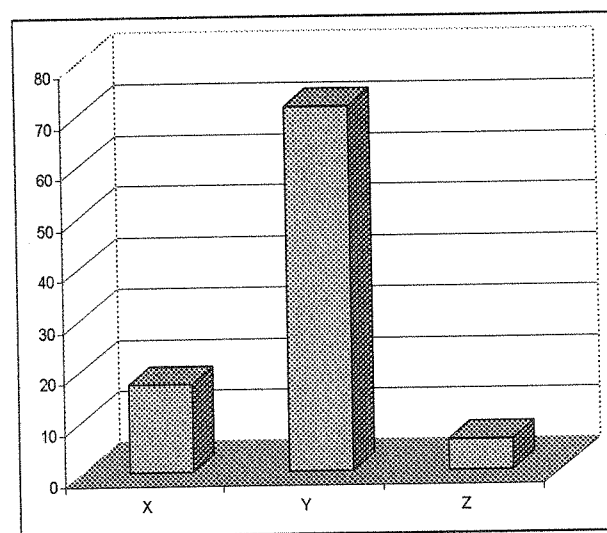


Figure 3: Contribution of parameters to the system response.

TABLE 4
PREPARATION CONDITIONS AND ACTIVITIES OF SOME DME SYNTHESIS CATALYSTS

Catalysts contents	Calcination Temp. (°C)	Precipitation agent	Mass ratio of γ -Al ₂ O ₃ to total metal oxides	Copper nitrate solution (Vol.%)	Zinc nitrate solution (Vol.%)	Al nitrate solution (Vol.%)	Slurry solution of γ -Al ₂ O ₃ (Vol.%)	*Activity ((mg DME)/g cat.hr)	DME selectivity (%)
CDME-1	350	Na ₂ CO ₃	0.5	47.45	28.99	0	23.56	6.26	87.2
CDME-2	350	Na ₂ CO ₃	0.5	27.84	34.28	17.01	20.86	3.442	86.8
CDME-3	350	Na ₂ CO ₃	0.5	20.10	29.70	31.21	18.99	3.298	86.2
CDME-4	350	Na ₂ CO ₃	0.5	15.02	29.58	37.30	18.11	2.793	85.8
CDME-5	350	Na ₂ CO ₃	0.5	41.73	18.48	18.48	21.31	9.314	86.9
CDME-6	350	Na ₂ CO ₃	0.5	40.56	36.18	0	23.26	4.288	87.2
CDME-7	350	Na ₂ CO ₃	0.5	21.11	22.60	37.99	18.30	4.708	86.1
CDME-8	350	Na ₂ CO ₃	0.5	22.60	32.25	25.42	19.73	3.212	86.5
CDME-9	350	Na ₂ CO ₃	0.5	36.08	12.51	31.78	19.63	12.86	86.0
CDME-10	350	Na ₂ CO ₃	0.5	26.18	18.28	36.89	18.64	6.839	86.3
CDME-11	350	Na ₂ CO ₃	0.5	41.72	34.97	0	23.31	4.563	87.2
CDME-12	350	Na ₂ CO ₃	0.5	31.78	35.52	11.02	21.69	3.632	87.0
CDME-13	350	Na ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	12.87	86.5
CDME-14	350	Na ₂ CO ₃	0.5	33.39	20.55	25.92	20.14	6.86	86.3
CDME-15	350	Na ₂ CO ₃	0.5	38.21	28.22	11.67	21.89	5.457	87.0
CDME-16	350	Na ₂ CO ₃	0.5	38.70	38.12	0	23.18	3.884	87.2
CDME-17	350	Na ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	12.87	86.5
CDME-18	350	(NH ₄) ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	14.27	84.9
CDME-19	350	(NH ₄) ₂ CO ₃	0.41	33.51	10.25	41.62	14.62	9.461	70.7
CDME-20	350	(NH ₄) ₂ CO ₃	0.56	30.54	9.33	37.93	22.21	11.91	84.8
CDME-21	300	(NH ₄) ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	10.28	86.5
CDME-22	500	(NH ₄) ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	3.761	78.9
CDME-23	700	(NH ₄) ₂ CO ₃	0.5	31.96	9.76	39.69	18.59	2.451	73.4

B. Kinetic study

The reaction has been carried out within the temperature range of 230-300 °C, 8 barg pressure and a wide range of catalyst to feed ratios. The results are presented in Figure 4 and Tables 5-8. The reaction rates given in these tables were calculated, assuming the plug flow of gas in the reactor, i.e.,

$$-r_{CO} = \frac{d(x_{CO})}{d\left(\frac{W}{F_{CO_0}}\right)} \quad (1)$$

$$r_{DME} = \frac{d\left(\frac{y_{DME,out} \cdot P}{RT}\right)}{d\left(\frac{W}{\phi_v}\right)}$$

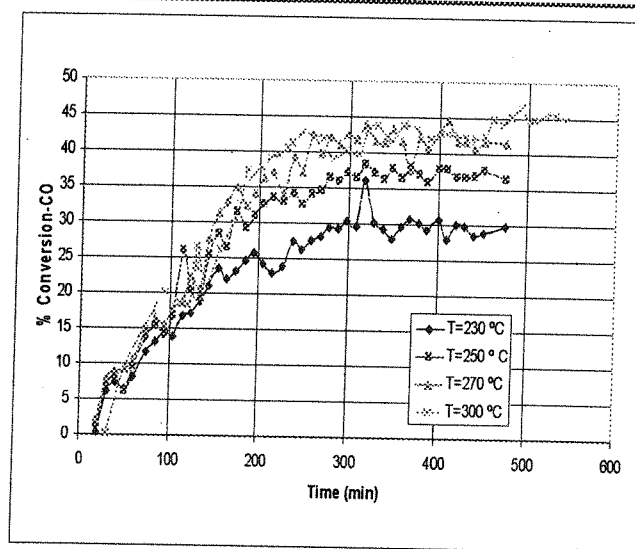


Figure 4: Conversion of CO as a function of time at different temperatures (W/F=1120 g/mol.min).

TABLE 5
DATA OF THE REACTOR'S OUTLET AT 230 °C

W_{cat}/F_{CO}	W_{cat}/ϕ_v	WHSV	P_{H_2}	P_{CO}	P_{CO_2}	P_{CH_3OH}	P_{DME}	P_{H_2O}	X_{CO}	$-r_{CO}$	r_{DME}
$gr/(mol/min)$	$gr/(m^3/min)$	hr^{-1}	barg	barg	barg	barg	barg	barg	%	$mol/(min.gr)$	$mol/(min.gr)$
260	3731	4.34	4.96	2.47	0.32	0.003	0.13	0.12	9.19	3.3E-04	1.5E-04
896	12658	1.26	4.60	2.29	0.48	0.03	0.30	0.30	24.67	1.2E-04	5.7E-05
1120	15873	1.03	4.55	2.26	0.46	0.04	0.35	0.34	31.33	1.0E-04	4.5E-05
1493	21052	0.75	4.43	2.20	0.52	0.07	0.40	0.36	32.94	7.4E-05	3.4E-05
1792	25316	0.63	4.39	2.17	0.51	0.09	0.43	0.41	33.30	6.3E-05	2.9E-05
2240	31746	0.5	4.34	2.15	0.49	0.13	0.45	0.44	34.62	5.3E-05	2.5E-05

TABLE 6
DATA OF THE REACTOR'S OUTLET AT 250 °C

W_{cat}/F_{CO}	W_{cat}/ϕ_v	WHSV	P_{H_2}	P_{CO}	P_{CO_2}	P_{CH_3OH}	P_{DME}	P_{H_2O}	X_{CO}	$-r_{CO}$	r_{DME}
$gr/(mol/min)$	$gr/(m^3/min)$	hr^{-1}	barg	barg	barg	barg	barg	barg	%	$mol/(min.gr)$	$mol/(min.gr)$
260	3731	4.34	4.91	2.45	0.33	0.004	0.16	0.15	11.01	3.2 E-4	2.2 E-4
896	12658	1.26	4.47	2.21	0.50	0.04	0.40	0.38	30.55	1.3E-4	8.8E-5
1120	15873	1.03	4.40	2.18	0.48	0.05	0.45	0.43	36.39	1.1 E-4	7.2E-5
1493	21052	0.75	4.24	2.1	0.56	0.08	0.52	0.5	37.83	8.7E-5	5.5E-5
1792	25316	0.63	4.18	2.06	0.55	0.11	0.56	0.54	40.27	7.6E-5	4.8E-5
2240	31746	0.5	4.11	2.02	0.53	0.16	0.60	0.58	42.61	6.5E-5	4.1E-5

TABLE 7
DATA OF THE REACTOR'S OUTLET AT 270 °C

W_{cat}/F_{CO}	W_{cat}/ϕ_v	WHSV	P_{H_2}	P_{CO}	P_{CO_2}	P_{CH_3OH}	P_{DME}	P_{H_2O}	X_{CO}	$-r_{CO}$	r_{DME}
$gr/(mol/min)$	$gr/(m^3/min)$	hr^{-1}	barg	barg	barg	barg	barg	barg	%	$mol/(min.gr)$	$mol/(min.gr)$
260	3731	4.34	5.00	2.39	0.40	0.003	0.14	0.07	16.50	4.7E-04	2.1E-04
896	12658	1.26	4.71	2.07	0.67	0.03	0.36	0.17	39.66	1.8E-04	8.3E-05
1120	15873	1.03	4.69	2.00	0.69	0.04	0.40	0.17	41.42	1.4E-04	6.8E-05
1493	21052	0.75	4.58	1.89	0.79	0.07	0.46	0.20	49.61	1.1E-04	5.1E-05
1792	25316	0.63	4.55	1.85	0.80	0.10	0.50	0.21	51.59	9.2E-05	4.4E-05
2240	31746	0.5	4.52	1.78	0.82	0.14	0.53	0.21	54.89	7.5E-05	3.8E-05

TABLE 8
DATA OF THE REACTOR'S OUTLET AT 300 °C

W_{cat}/F_{CO}	W_{cat}/ϕ_v	WHSV	P_{H_2}	P_{CO}	P_{CO_2}	P_{CH_3OH}	P_{DME}	P_{H_2O}	X_{CO}	$-r_{CO}$	r_{DME}
$gr/(mol/min)$	$gr/(m^3/min)$	hr^{-1}	barg	barg	barg	barg	barg	barg	%	$mol/(min.gr)$	$mol/(min.gr)$
260	3731	4.34	5.06	2.35	0.44	0.003	0.13	0.01	19.88	3.7E-04	1.7E-04
896	12658	1.26	4.86	1.97	0.78	0.03	0.33	0.30	42.32	1.3E-04	7.0E-05
1120	15873	1.03	4.87	1.89	0.82	0.04	0.37	0.01	44.7	1.0E-04	5.9E-05
1493	21052	0.75	4.80	1.76	0.94	0.07	0.43	0.003	55.80	7.6E-05	4.6E-05
1792	25316	0.63	4.78	1.71	0.96	0.09	0.46	0.003	57.99	6.6E-05	4.0E-05
2240	31746	0.5	4.74	1.63	0.98	0.13	0.50	0.01	61.31	5.4E-05	3.3E-05

A number of studies on syngas transformation into liquid hydrocarbons have been made (Erena *et al.* [16], X. D. Peng *et al.* [17], G. Bercic *et al.* [18], [19] and Graff *et al.* [20]-[22]). A method similar to those proposed by Graff and Bercic for complex reactions in isothermal fixed bed micro reactors was adopted in the present study. The Graff kinetic model has been used for the transformation of syngas to methanol and that of Bercic has been applied in the synthesis of DME from methanol. These are as follows:

a- Graff model:

$$-r_{CO} = \frac{k_1 [P_{CO} \cdot P_{H_2}^{3/2} - P_{CH_3OH} / (P_{H_2}^{1/2} \cdot k_{P1})]}{(1 + k_2 P_{CO} + k_3 P_{CO_2}) (P_{H_2}^{1/2} + k_4 P_{H_2O})} \quad (3)$$

b- Bercic model:

$$r_{DME} = \frac{-k_5 (P_{CH_3OH}^2 - P_{H_2O} \cdot P_{DME} / K_{P2})}{(1 + 2(k_6 P_{CH_3OH})^{1/2} + k_7 P_{H_2O})^4} \quad (4)$$

Estimation of values for the kinetic parameters involved minimization of error. Using the nonlinear regression analysis and applying the results presented in Tables 6-9 to the relations 3 and 4, the kinetic parameters have been calculated. The data are given in Table 9.

TABLE 9
KINETIC PARAMETERS

Kinetic constant	Temperature (°C)				K ₀₁	E/R
	230	250	270	300		
K ₁	8.68E-06	4.2E-05	2.6E-05	1.21E-05	1.1E-11	-7963.0
K ₂	0.23479	0.32373	0.44512	0.54672	2.9E+02	3561.6
K ₃	5.56758	3.32369	1.16417	0.94748	9.6E-07	-7812.4
K ₄	4.95952	3.39190	0.25811	0.01013	8.2E-23	-26755.0
K _{P1}	0.02704	0.02108	0.01194	0.00708	2.5E-07	-5855.5
K ₅	0.00766	0.00565	0.00364	0.001	6.1E-10	-8322.8
K ₆	7.7855	11.0551	31.29	46.7116	5.4E+07	7940.1
K ₇	8.38936	6.81023	6.19	5.13949	1.7E-01	-1957.2
K _{P2}	0.02262	0.01735	0.00843	0.00742	1.3E-06	-4880.6

4. CONCLUSION

In the present study, the activities of DME synthesis catalysts were gradually improved during a four phase preparation program and the following observations were made:

By applying the Taguchi method and analysis of data, certain interactions between the preparation parameters were noted. The appropriate experimental conditions, predicted from Taguchi method were (X4, Y1, Z4).

ZnO was found to have the greatest impact on the catalysts activity.

The catalysts prepared using ammonium carbonate as the precipitant were more active in comparison with those applying sodium carbonate.

The highest activity was obtained with a catalyst containing 50 weight percent of γ -alumina and calcinated at 350 °C.

A kinetic expansion for syngas transformation to DME based on Graff methanol synthesis and Bercic dehydration models has been derived and correlated with the experimental results over a range of temperatures. The degree of agreement between the two sets of data was 90-95%.

5. NOMENCLATURE

F	Molar flow rate (mol/min)
k	Kinetic parameters
K _p	Equilibrium constant
P	Pressure (barg)
r	Reaction rate (mol/min.g _{cat.})
R	Constant of gases (J/mol.K)
T	Temperature (K)
W	Catalyst mass (g)
x	Conversion
X	Concentration of copper oxide
y	Mol fraction
Y	Denotes concentration of zinc oxide
Z	Denotes concentration of aluminum oxide

Greek letters

ϕ_v	Volumetric flow (m ³ /min)
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6. REFERENCES

- [1] John BØgild Hansen, Bodil Voss, Finn Joensen, Inga Dera - Siguroa-vdottir, "Large Scale Manufacture of Dimethyl Ether a New Alternative Diesel Fuel From Natural Gas", *SAE Technical Paper Series, International Congress & Exposition, Detroit, Michigan, February 27-March 2 1995*.
- [2] G. Sam Samdani, "Chementator", *Chem. Eng.*, pp.17-18, April 1995.
- [3] Theo Fleisch, Chris McCarthy, Arun Basu, Carl Udovich, "Demonstration of ULEV Emissions on a Navistar Diesel Engine Fueled with Dimethyl Ether", *SAE Technical Paper Series, International Congress & Exposition, Detroit, Michigan, February 27-March 2 1995*.
- [4] Z. Nle, H. Liu, D. Liu, W. Ying, D. Fang, "Intrinsic Kinetics of Dimethyl Ether Synthesis From Syngas", *J. of Natural Gas Chemistry*, vol. 14, pp. 22-28, 2005.
- [5] Q. Ge, Y. Huang, F. Qiu, S. Li, "Bifunctional catalysts for conversion of synthesis gas to DME", *Applied Catalysis*, vol.167, pp. 23-30, 1998.
- [6] D. Mao, W. Yang, J. Xia, B. Zhang, Q. Song, Q. Chen, "Highly Effective Hybrid Catalyst for the Direct Synthesis of DME from Syngas with Maynesium Oxide-Modified Hzsm-5 as Dehydration Component", *Journal of Catalysis*, vol. 230, pp. 140-149, 2005.
- [7] K. Sun, W. Lu, F. Qiu, S.Liu, X. Xu, "Direct Synthesis of DME over Bifunctional Catalyst: Surface Properties and Catalytic Performance", *Applied Catalysis*, vol. 252, pp. 243-249, 2003.
- [8] J. H. Kim, M.J. Park, S. J. Kim, O. S-Joo, K. D. Jung, "DME Synthesis From Syngas on the Admixed Catalysts of Cu/ZnO/Al₂O₃ and ZSM-5", *Applied Catalysis*, vol. 264, pp. 37-41, 2004.
- [9] G. Qi, X. Zheng, J. Fei, z. Hou, "A Novel Catalyst for DME Synthesis from CO Hydrogenation", *J. Molecular Catalysis*, vol. 176, pp. 195-203, 2001.
- [10] J. L. Li, X. G. Zhang, T. Inui, "Improvement in the Catalyst Activity for Direct Synthesis of DME From Syngas Through Enhaneing the dispersion of CuO/ZnO/ γ -Al₂O₃ in Hybrid Catalyst", *Applied Catalysis*, 147 (1996), 23-33.
- [11] A. Hadipour, "Catalyst Preparation, Determination of Kinetic parameters and Reactor Modeling of Direct Synthesis of DME from Syn.gas", Ph.D. dissertation, Dept. Chem. Eng., Univ. Amir Kabir, 2006.
- [12] Taguchi G., Konishi S., *Orthogonal Arrays and linear Graphs*. Dearborn, MI: American Supplier Institute Press; 1987.
- [13] R. A. Fisher, *Statistical Methods for Research workers*, Oliver & Boyd, London, 1952.
- [14] M. Xu, J.H. Lunsford, D.W. Goodman, A. Bhattacharyya, "Synthesis of DME From Methanol Over Solid Acid Catalysts", *Applied Catalysis*, vol.149, pp. 289-3-1, 1997.
- [15] M. Sohrabi, A. Irandokht, "Synthesis and Activity Measurement of some Water Gas Shift Reaction Catalysts", *Reac. Kinet. Catal. Lett.*, vol. 80, no. 2, pp. 303-309, 2003.
- [16] J.Erena, J. M. Arandes, J. Bilbao, A. G. Gayubo, H. I. De lasa, "Conversion of Syngas to Liquid Hhydrocarbons Over a Two-Component (Cr₂O₃-zno and zsm-5 zeolite) Catalyst: Kinetic Modeling and Catalyst Deactivation", *Chem. Eng. Sci.*, vol. 55, pp. 1845-1855, 2000.
- [17] X. D. Peng, B. A. Toseland, P. J. A. Tijn, "Kinetic Understanding of Chemical Synergy under LPDME Conditions - Once Through Applications", *Chem. Eng. Sci.*, vol. 54, pp. 2787-2792, 1999.
- [18] G. Bercic, J. Levec, "Intrinsic and Global reaction rate of Methanol Dehydration Over γ -Al₂O₃ Pellets", *Ind.Eng. Chem. Res.*, vol. 31, pp. 1035-1040, 1992
- [19] G. Bercic, J. Levec, "Catalytic Dehydration of Methanol to DME. Kinetic Investigation and Reactor Simulation", *Ind. Eng. Chem. Res.*, vol. 32, pp., 2478-2484, 1993.
- [20] G. H. Graaf, J. G. M. Winkelman, E. J. Stamhuis, A. A. C. M. Beenakers, "Kinetics of Three Phase Methanol Synthesis", *Chem. Eng. Sci.*, vol. 43, no 8, pp.2161-2168, 1988.
- [21] G. H. Graaf, P. J. J. M. Sijtsema, E. J. Stamhuis, G. E. H. Joosten, "Chemical Equilibria In Methanol Synthesis", *Chem. Eng. Sci.*, vol. 41, no. 11, pp. 2883-2890, 1986.
- [22] G. H. Graaf E. J. Stamhuis, A. A. C. M. Beenakers, "Kinetics of Low-Pressure Methanol Synthesis", *Chem. Eng. Sci.*, vol. 43, no 12, pp. 3185-3195,1988.