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Research Note

Preparation of Some Bifunctional Catalysts for Direct Conversion of Synthesis Gas to Dimethyl Ether

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In the present study, twenty three catalysts for dimethylether (DME) synthesis were prepared, according to a pre-designed research program consisting of four phases. In each phase, by applying the Taguchi experimental design method, a number of catalysts was synthesized by the co-precipitation method, using different percentages of metal nitrate solution. The activities of the catalysts were determined by applying a laboratory scale continuous packed bed reactor. It was noted that the ZnO content of the catalyst, nature of precipitant agent, mass ratio of gamma-alumina to total metal oxides and calcination temperature, had the highest impact on the activity of the catalysts.

INTRODUCTION

Dimethyl ether (DME) is an intermediate in the preparation of a number of industrial chemicals. It has also found an increasing application in the aerosol industry as an ozone friendly propellant. In addition, DME is used as an ultra-clean fuel for diesel engines [1-3].

Commercial production of dimethylether 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 synthesis 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 site used for methanol formation and methanol dehydration, respectively. These catalysts usually contain zinc, copper and aluminum oxides (for methanol formation) and gamma-alumina (for methanol dehydration) and are prepared by the co-precipitation method [5].

DME can be obtained directly from synthesis gas, according to the following reactions:

I) $CO + 2H_2 \Leftrightarrow CH_3OH$ (methanol synthesis),

II) $CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$ (methanol synthesis),

III) $CO + H_2O \Leftrightarrow CO_2 + H_2$ (water gas shift reaction),

IV) $2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$ (dehydration of methanol to DME),

V) $2CO + 4H_2 \Leftrightarrow CH_3OCH_3 + H_2O$ (direct synthesis of DME).

In the present study, the synthesis and activity measurement of some DME catalysts were performed within a program consisting of four phases. In the first phase, according to the Taguchi experimental design method [6], sixteen catalyst 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 its constituents were presented.

EXPERIMENTAL

Material

The chemicals used in the present study were all analytical grade and supplied by Merck and BASF, in Germany. These were: Copper nitrate

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[$Cu(NO_3)_2.3H_2O$], zinc nitrate [$Zn(NO_3)_2.6H_2O$], aluminum nitrate [$Al(NO_3)_3.9H_2O$], sodium carbonate [Na_2CO_3] and ammonium carbonate [$(NH_4)_2CO_3$].

Catalyst Preparation

A solution of $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$ 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 was then filtered and washed several times with deionized water to remove residual sodium ions and added to a suspended liquid having a 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 BET surface area of the catalyst was measured using a Quantasorb apparatus (from the Quantachrome Company). The XRF and XRD patterns of the catalysts were also determined.

Activity Measurement

Catalytic activity of all samples in converting synthesis gas to DME were studied under steady state conditions in a fixed bed flow reactor (i.d., 6.4 mm and length 650 mm) connected, on line, to a GC apparatus. The catalyst was packed in a stainless steel tube equipped with a thermocouple in the catalyst bed. All the experiments were performed at 250°C and a constant pressure of 8 barg. Prior to catalytic testing, the samples were crushed and sieved to fine powder. In each experimental run, about 2 grams of catalyst (grain size equal to 150 μm) were loaded into 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 purged with nitrogen and then pressurized. The catalysts were reduced in flowing hydrogen gas diluted with nitrogen.

A mixture of 4 vol. % CO_2, 32 vol. % CO and 64 vol. % H_2, with a space velocity of 6000 hr ^{1}, entered the top section of the reactor that acted as a pre-heater. Three mass flow meters (Brooks, Model 5850) and a control system were used to monitor the

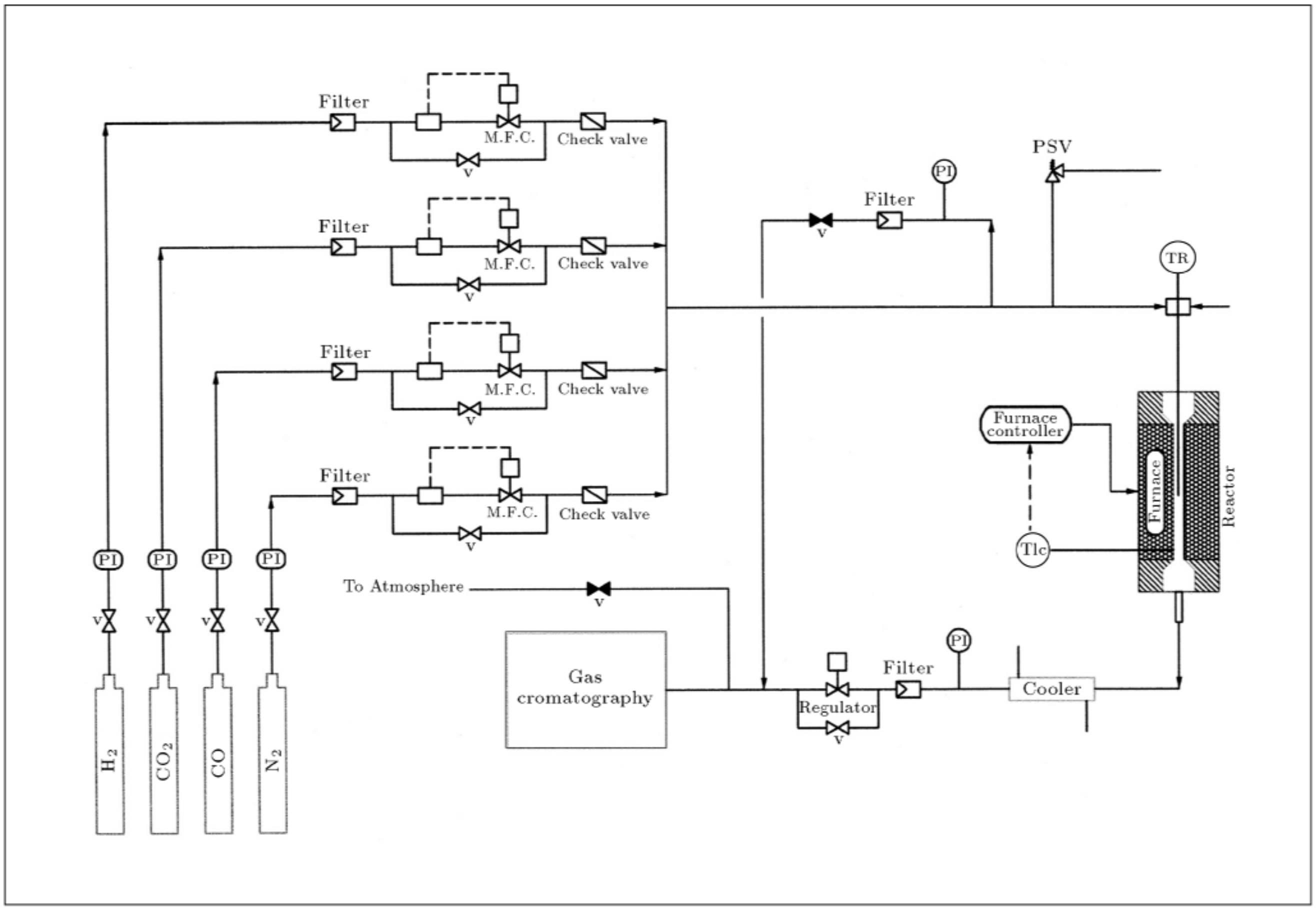

Figure 1. Schematic diagram of the reactor setup.

individual gas flow rates and to provide the required gas mixtures.

When steady state conditions were established, 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 minute 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 cm^3/min. The thermal conductivity detector was applied.

RESULTS AND DISCUSSION

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 [6]. Arrangements of the parameters and the related levels are shown in Table 1.

Table 1. Arrangement of parameters in L-16 presentation.

Test/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

Sixteen samples (CDME-1–CDME-16) were prepared and, accordingly, sixteen experimental programs were performed, from which the optimum conditions were determined. These are shown in Table 2. In the above runs, the final activity of the 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 parameter 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 the analysis are presented in Table 3. The latter indicate 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 the catalyst [7].

Basically, a larger response corresponds to a better catalyst characteristic. However, the relative importance, from among the catalyst preparation parameters of the performance characteristic still needs to be known, so that optimal combinations of catalyst preparation parameter levels can be determined more accurately. By considering the above observation, the optimum conditions for the catalyst synthesis were determined to be $X4$, $Y1$ 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 the above three parameters upon the final activity of the catalyst is as ZnO>CuO>Al_2O_3. In addition, the F-test [8] can also be used to determine which catalyst preparation

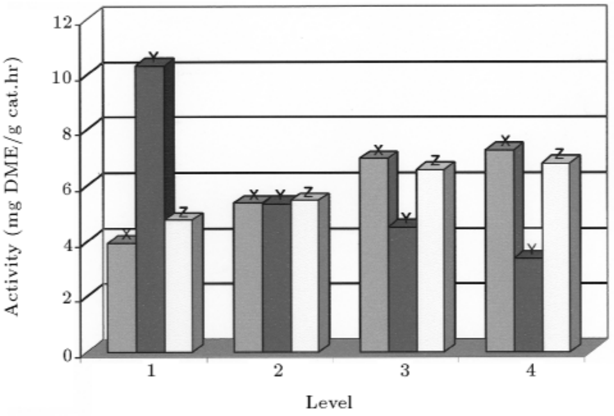

Figure 2. Average system response to parameters at various levels.

Table 2. Preparation conditions and activities of some DME synthesis catalysts.

Catalysts Contents	Calcination Temp. (°C)	Precipitation Agent	Mass Ratio of γ - Al_2O_3 to Total Metal Oxides	Copper Nitrate Solution (Vol.%)	Zinc Nitrate Solution (Vol.%)	Al Nitrate Solution (Vol.%)	Slurry Solution of γ - Al_2O_3 (Vol.%)	*Activity ((mg DME)/ g cat.hr)	DME Selectivity (%)
CDME-1	350	Na_2CO_3	0.5	47.45	28.99	0	23.56	6.26	87.2
CDME-2	350	Na_2CO_3	0.5	27.84	34.28	17.01	20.86	3.442	86.8
CDME-3	350	Na_2CO_3	0.5	20.10	29.70	31.21	18.99	3.298	86.2
CDME-4	350	Na_2CO_3	0.5	15.02	29.58	37.30	18.11	2.793	85.8
CDME-5	350	Na_2CO_3	0.5	41.73	18.48	18.48	21.31	9.314	86.9
CDME-6	350	Na_2CO_3	0.5	40.56	36.18	0	23.26	4.288	87.2
CDME-7	350	Na_2CO_3	0.5	21.11	22.60	37.99	18.30	4.708	86.1
CDME-8	350	Na_2CO_3	0.5	22.60	32.25	25.42	19.73	3.212	86.5
CDME-9	350	Na_2CO_3	0.5	36.08	12.51	31.78	19.63	12.86	86.0
CDME-10	350	Na_2CO_3	0.5	26.18	18.28	36.89	18.64	6.839	86.3
CDME-11	350	Na_2CO_3	0.5	41.72	34.97	0	23.31	4.563	87.2
CDME-12	350	Na_2CO_3	0.5	31.78	35.52	11.02	21.69	3.632	87.0
CDME-13	350	Na_2CO_3	0.5	31.96	9.76	39.69	18.59	12.87	86.5
CDME-14	350	Na_2CO_3	0.5	33.39	20.55	25.92	20.14	6.86	86.3
CDME-15	350	Na_2CO_3	0.5	38.21	28.22	11.67	21.89	5.457	87.0
CDME-16	350	Na_2CO_3	0.5	38.70	38.12	0	23.18	3.884	87.2
CDME-17	350	Na_2CO_3	0.5	31.96	9.76	39.69	18.59	12.87	86.5
CDME-18	350	$(NH_4)_2CO_3$	0.5	31.96	9.76	39.69	18.59	14.27	84.9
CDME-19	350	$(NH_4)_2CO_3$	0.41	33.51	10.25	41.62	14.62	9.461	70.7
CDME-20	350	$(NH_4)_2CO_3$	0.56	30.54	9.33	37.93	22.21	11.91	84.8
CDME-21	300	$(NH_4)_2CO_3$	0.5	31.96	9.76	39.69	18.59	10.28	86.5
CDME-22	500	$(NH_4)_2CO_3$	0.5	31.96	9.76	39.69	18.59	3.761	78.9
CDME-23	700	$(NH_4)_2CO_3$	0.5	31.96	9.76	39.69	18.59	2.451	73.4

(*): Activities were determined at 250°C and 8 barg.

Table 3. 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	-

parameters have a significant effect on the performance characteristic. From the Fisher tables [8], with 95% confidence, $F_{0.05,3,6}$ was found to be 4.76. The F values for X, Y and Z obtained from the Taguchi method were 16.80, 66.85 and 6.52, respectively. These are greater than the corresponding values in the Fisher tables. The tests are, therefore, reliable with 95% confidence. It seems that these parameters have a great impact on the performance characteristics of the catalyst prepared. The calculation error was 5.426%.

Referring to Figure 2, it may be observed that an excess of ZnO in catalysts has a negative effect on the activity, while the presence of CuO and Al_2O_3 enhances the catalyst activity. These findings could be explained by noting that the presence of copper and aluminum oxides increases the dispersion of active sites and, hence, promotes the surface area of the 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 4.

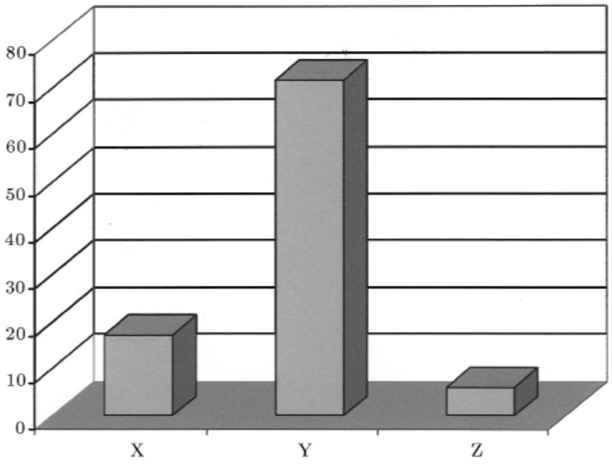

Figure 3. Contribution of parameters to the system response.

In the second phase, the effect of precipitant nature (sodium carbonate and ammonium carbonate) on catalyst activity was studied. Two more samples (CDME-17 and 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 catalyst activity. The Na^+ ions could reduce the number of acid sites of the dehydration component (γ-alumina) of the catalyst [9] 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 and 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 oxide phase.

Finally, in the fourth phase, the effect of calcination temperature on catalyst 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 the case of a 350°C calcination temperature (CDME-18, CDME-21 - CDME-23). This may be explained by assuming that, at higher calcination temperatures, partial sintering of catalyst particles could occur and the active area of the catalyst is reduced. Sohrabi et al. [10] have reported a similar observation, stating that, with an increase in calcination temperature, the copper crystallite particle size increases and acts as the backbone of the water gas shift reaction.

Catalyst activity was measured as the mg of DME formed per hour per gram of catalyst. These are presented in Table 2. In Table 4, some further properties of some catalysts are given.

CONCLUSION

In the present study, the activities of DME synthesis catalysts were gradually improved during a four-phase

Table 4. Certain properties and activities of some DME synthesis catalysts.

Catalyst Name	Calcination Temperature (°C)	Total Surface Area (BET) (m^2/g cat)	Major Crystalline Phases	*Activity (mg DME)/ (g Catalyst.h)
CDME-1	350	143.24	CuO, ZnO, Al_2O_3	6.26
CDME-4	350	121.14	CuO, ZnO, Al_2O_3	2.79
CDME-5	350	146.76	CuO, ZnO, Al_2O_3	9.31
CDME-8	350	124.39	CuO, ZnO, Al_2O_3	3.21
CDME-9	350	240.32	CuO, ZnO, Al_2O_3	12.87
CDME-12	350	150.72	CuO, ZnO, Al_2O_3	3.63
CDME-13	350	251.32	CuO, ZnO, Al_2O_3	12.87
CDME-16	350	130.25	CuO, ZnO, Al_2O_3	3.88
CDME-18	350	257.46	CuO, ZnO, Al_2O_3	14.27
CDME-22	500	-	CuO, ZnO, Al_2O_3	3.76
CDME-23	700	65.25	CuO, ZnO, Al_2O_3	2.45

(*): Activities were determined at 250°C and 8 barg.

preparation program and the following observations were made:

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

b. ZnO was found to have the greatest impact on catalyst activity;

c. The catalysts prepared, using ammonium carbonate as the precipitant, were more active in comparison to those applying sodium carbonate;

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

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