Two-level Full Factorial Design for Selectivity Modeling and Studying Simultaneous Effects of Temperature and Ethanol Concentration in Methanol Dehydration Reaction

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Using surface analysis, simultaneous effects of temperature (260-380 ℃) and ethanol concentration (0-1%) on dimethyl ether (DME) selectivity, yields of hydrocarbon and DME, and methanol conversion were investigated in methanol dehydration reaction over γ-Al$_2$O$_3$ catalyst. Methanol conversion and yield of hydrocarbon/DME were found to be significantly affected by temperature and the temperature-ethanol concentration interactions. In addition, DME selectivity and yield of DME were found to be influenced by the process temperature, and ethanol concentration as well as their interactions. BET surface area measurement and scanning electron microscopy technique (SEM) confirmed that the catalyst deactivation was intensified at higher temperatures by increasing ethanol concentration. Using statistical regression, a mathematical model was developed, and then validated, to describe simultaneous effects of temperature and feedstock ethanol concentration on DME selectivity. Although the model was statistically significant, curvature was not significant. Therefore, a two-level full factorial design of experiment approach was followed as a promising strategy for DME selectivity modeling and interpretation of the data in this work.

Keywords: Dimethyl ether, Two-level factorial experiment, Surface analysis, Selectivity modeling, Ethanol concentration, Catalyst deactivation

INTRODUCTION

Ever increasing consumption of oil-based fuels has been associated with serious environmental problems while dwindling petroleum reserves worldwide. Furthermore, increasing demand for energy and fluctuation of crude oil prices encouraged governments to look for cleaner and cheaper sources of energy. Having a nearly high cetane number (55-60), and zero sulfur content with low NO$_x$ emission, dimethyl ether is an excellent non-petroleum clean fuel [1]. It can be used as an alternative fuel for both compression ignition engines and household applications in coming decades [2,3].

DME is known as a non-toxic and non-carcinogenic volatile organic compound [4,5]. Due to its lower globe warming potential (GWP) and zero ozone depletion potential (ODP), DME is widely used as an alternative to chlorofluorocarbon (CFC) in environment-friendly aerosol sprays and green refrigerants [6]. It is further used as an alternative aerosol propellant to CFC and liquefied petroleum gas (LPG) in the cosmetic industry [7]. According to the similarities in physical properties between DME and LPG, DME may be applied either as an alternative to LPG for household applications or as an additive for LPG-driven engines [4]. Due to increasing market demand for some valuable chemicals such as light olefins, aromatics and hydrogen, DME, as a non-petroleum-based raw material, has attracted a large deal of attention

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from many researchers [8-10]. Then, in order to meet the future market, there would be a growing potential demand for the large-scale production of DME.

Industrially speaking, DME is usually produced *via* either of two approaches. The traditional approach is considered as an indirect method, by which DME is produced via methanol dehydration reaction over a solid acid catalyst such as alumina, zeolite, *etc.* [11,12].

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad (1)$$

The methanol itself is initially produced through a catalytic reaction of synthesis gases (CO and H_2)

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (2)$$

More recently, some research activities have been performed to merge these two reactions in a catalytic reactor, using simultaneous catalysis of methanol synthesis and dehydration [13]. This approach is considered as a direct method or STD (Syngas To DME) [14].

An extensive deal of attention has been focused on preparing catalysts of high selectivity toward DME coupled with low yield of hydrocarbon production. Moreover, effects of such parameters as temperature, pressure, space velocity, and weight ratio of methanol synthesis catalyst to dehydration catalyst on the selectivity towards DME have been investigated by scholars [15,16]. Erena *et al.* studied effects of operating conditions on the synthesis of DME over a bifunctional CuO-ZnO-Al$_2$O$_3$/NaHZSM-5 catalyst in a fixed-bed reactor. They found the optimum conditions for the formation of DME as follows: T = 275 ℃, P = 40 bar, H_2/CO = 2/1 and space time = 67 (g of catalyst) h mol^{-1} of (H_2 + CO). Furthermore, increasing the temperature above 275 ℃ decreased CO conversion and DME selectivity due to thermodynamic restrictions of the exothermal reaction and loss of catalyst activity due to Cu sintering [17]. Another research group investigated various dehydration catalysts under diverse sets of operating conditions in direct STD [18]. The influence of the operating conditions was found to be dependent on the type of catalysts, *i.e.* a rise of temperature led to enhanced conversion when γ-Al$_2$O$_3$ was used as dehydration catalyst, such that the maximum conversion was obtained at 250 ℃. On the other hand,

zeolites did not produce such a maximum within the investigated temperature range. For H-MOR90 and H-MFI90 catalysts, a rise of temperature decreased the selectivity towards DME. The effect of water was also studied over Cu/ZnO/Al$_2$O$_3$-γ-Al$_2$O$_3$ catalysts, with no deactivation indicated at water contents below 10%. These studies were, however, conducted based upon the so-called "one-factor-at-a-time" approach, whose major disadvantage is failure to consider possible interactions among the studied parameters. Hence, design of experiments (DOE) strategy is noticeable when it comes to factor screening or optimization. Factorial design of experiment is not only used primarily for screening significant factors, but it can also be sequentially applied to model and refine a given process. When the objective of the experiment is factor screening or process characterization, it is usually best to keep the factor levels low. Two-level factorial design is recommended for factor studying, screening, and modeling when the experiments are expensive or difficult to perform [19]. For instance, Farias *et al.* used the strategy to study dependencies of the product distribution in Fischer-Tropsch synthesis on operating pressure and temperature for an un-promoted iron catalyst as well as a potassium-promoted one [20]. The application of Taguchi method in the direct STD has been addressed in some papers [3,21], as of preparing this manuscript, a report on the application of a two-level factorial design in indirect DME synthesis is yet to be released. However, it is still important to study the effects of different parameters on selectivity toward DME in this method [22,23].

Catalyst deactivation usually affects the DME selectivity through such mechanisms as coking, sintering of active sites, blockage of acidic sites by water and poisoning by impurities in the syngas [17]. Blocking the catalyst active sites by carbonaceous residues (coking), the access of reactant molecules is restricted during the reaction [24]. Catalyst deactivation by coking can be promoted by increasing the DME concentration in the feed and considerably restricted by a lower water formation (below 10%) [25]. On the other hand, higher water content in the synthesis gas feed can limit the DME production by site blocking [18]. In an industrial indirect method of DME production, feedstock usually contains low amounts of ethanol (0-1%), which may influence the selectivity toward

DME and the catalyst performance. In this paper, effects of ethanol concentration on DME selectivity, methanol conversion, yield of DME, and yield of hydrocarbons/DME were investigated, in different industrial temperatures, over a gamma alumina catalyst using a 2^2 full factorial design with two center points. Furthermore, based on a statistical regression approach, an empirical model was proposed for DME selectivity and validated by using experimental data.

EXPERIMENTAL

Materials

Being of analytical grade, nitrogen (purity of 99.99%), ethanol (purity of 99.99%) and methanol (purity of 99.99%) were obtained from Merck. Gamma alumina was applied as the catalyst of dehydration reaction. Details of the catalyst preparation and characterization and the analytical method have been reported elsewhere [3].

Experimental Apparatus and Method

Figure 1 illustrates a schematic representation of the experimental setup. All gas lines to the reactor bed were made up of stainless steel tubing. A mass flow controller (Bronkhorst HI-TECH, EL-FLOW) was used to automatically adjust the input flow rate of nitrogen.

Methanol and ethanol were supplied from the separate feed tanks and controlled by mini-metering pumps. The mixture of input gases was then introduced into a mixer and pre-heater at 250 ºC. The temperature of the downstream effluent was constantly maintained above 150 ºC, so as to avoid the possible condensation of water, methanol, or DME. The dehydration reaction was carried out in a tubular fixed-bed micro-reactor equipped with four temperature indicator controllers (TICs). The reactor consisted of a single stainless steel tube with an inner diameter of 9 mm and a back-pressure regulator (BPR) to control total bed pressure of the desired process; the BPR could be operated at pressures ranging from atmospheric pressure to 700 psig. Prior to the catalytic measurements, the samples were crushed, sieved (to 25-40 mesh size), and then heated *in situ*, at a heating rate of 5 K min^{-1} under a 50 ml min^{-1} flow of N$_2$ at 220 ºC for 2 h under atmospheric pressure. In each experiment, 1 g of the catalyst was tested at a pressure of 16 bar, with the methanol flow rate being 0.55 ml min^{-1}. The ranges of temperature (260-380 ºC) and ethanol concentration (0-1%) were chosen according to the two-level factorial design of experiment. A small portion of the reactor effluent was subjected to gas chromatography (GC) for online analysis. The reaction performance results, including methanol conversion, DME selectivity, and yields
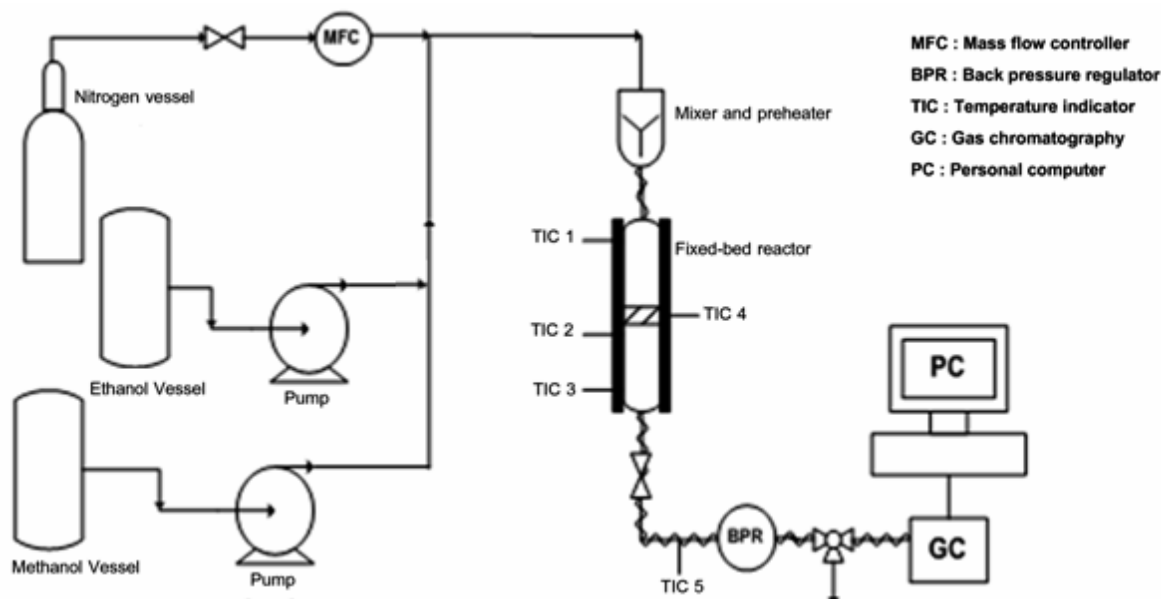

Fig. 1. Schematic representation of the reactor in methanol dehydration reaction.

Table 1. Experimental Level of the Independent Variables

Independent variable	Unit	Symbol	Low (-1)	Center (0)	High (+1)
Temperature	ºC	A	260	320	380
Ethanol concentration	%	B	0	0.5	1

Table 2. Actual/Coded Values of the Independent Variables Using 2^2 Full Factorial Design with 2 Center points

Run	Temperature ©		Ethanol concentration	
	Coded	Actual	Coded	Actual
1	1	380	1	1
2	1	380	-1	0
3	-1	260	1	1
4	0	320	0	0.5
5	-1	260	-1	0
6	0	320	0	0.5

Table 3. Experimental Results (%) According to Design Arrangement

Run	Conversion to DME	DME selectivity	Yield of DME	Yield of hydrocarbon & DME
1	91.1826	92.0613	84.8780	91.0817
2	93.4405	97.1889	93.0111	93.4308
3	56.4887	99.2563	56.2887	56.3523
4	89.7464	97.6940	88.7263	89.7319
5	53.9912	99.9798	53.9720	53.9818
6	89.8231	97.3500	88.2771	89.6200

of DME and hydrocarbons were calculated subsequently.

Design of Experiments

Ethanol concentrations in the feedstock and process temperature were the two independent factors investigated herein. In order to choose the factor limits shown in Table 1, various experiments were carried out considering the conditions of industrial indirect DME synthesis.

Using a two-level full factorial DOE with two center points, 6 runs were proposed as presented in Table 2. In order to normalize error distribution, the experiments were ordered randomly. All the independent factors applied in the DOE were coded according to the Eq. (3):

$$X_i = \frac{X_i - X_0}{\Delta X_i} \qquad (3)$$

where, x_i is the coded value and x_0 is the real value of the considered independent variable at the center point.

Indeed, the coded values of +1, 0 and -1 referred to high level, center point, and low level of each variable, respectively. Methanol conversion, yield of DME and hydrocarbons, and DME selectivity were calculated as follows:

$$Conversion = \frac{\left[F_{CH_3OH_{inlet}} - F_{CH_3OH_{outlet}} \right]}{F_{CH_3OH_{inlet}}} \times 100 \qquad (4)$$

$$Yield\ of\ DME\ or\ Hydrocarbons = \frac{\left[F_{DME\ or\ Hydrocarbon} \right]}{F_{CH_3OH_{inlet}}} \times 100 \qquad (5)$$

$$DME\ Selectivity = \frac{\left[F_{DME} \right]}{\left[F_{CH_3OH_{inlet}} - F_{CH_3OH_{outlet}} \right]} \times 100 \qquad (6)$$

where, F terms are molar flow rates of different components.

RESULTS AND DISCUSSION

Performing six experiments in a random order, the results were revealed as presented in Table 3. The variability in responses might be due to experimental error, effects of factors or their interactions. Therefore, sources of these changes were investigated using statistical surface analysis and analysis of variance (ANOVA).

Statistical Surface Analysis

Effects of temperature on the responses are shown in Figs. 2a-d. By increasing the temperature from 260 to 380 ºC, methanol conversion and yields of DME and hydrocarbon were increased, while DME selectivity was decreased.

In all runs, the ratio of catalyst weight to feedstock flow (W/F) was constant. As a result, the ratio of methanol conversion to the rate of reaction (x/r) would be constant. Hence, a rise of temperature increased the reaction rate, leading to enhanced DME conversion. However, the methanol dehydration reaction is a reversible and exothermic process. Both the methanol conversion and yield of DME were observed to increase with increasing the temperature within the temperature range of 260-380 ºC, beyond which range, they decreased by further increasing in the temperature.

Although the amounts of undesired products (hydrocarbons) were lower at 260 ºC, methanol conversion was at its lowest level at this temperature. Therefore, the low temperature (260 ºC) was recognized as unsuitable for the methanol dehydration reaction over gamma alumina catalyst. By increasing the temperature to 380 ºC, the yield of hydrocarbons (*e.g.* methane, ethane, ethene, and propene) was increased. The occupation of active sites on the catalysts by these hydrocarbons prevents methanol from being absorbed on these sites. Referred to as coking, this phenomenon results in decreased selectivity towards DME.

Figures 3a-d shows the effects of ethanol concentration in the feedstock on the responses. According to Figs. 3d and c, ethanol concentration was of no significant effects on the conversion to DME and yield of hydrocarbon and DME production, individually. On the other hand, increasing ethanol concentration decreased the DME selectivity due to the occupation of the active sites on the catalysts.

In order to study the simultaneous effects of temperature and ethanol concentration, surface analysis methodology was used, with the results presented in Figs. 4a-c. An increasing in ethanol concentration decreased DME selectivity (Fig. 4a), yield of DME and hydrocarbons (Fig. 4b), and yield of DME (Fig. 4c) with greater slopes at higher temperatures. In a catalytic reaction, desired and undesired products are usually generated through parallel reactions over active sites of catalysts. In DME production, some of these sites would be occupied by the existing ethanol in the feedstock. This problem would be intensified with temperature. Additionally, the coking problem would be more severe at higher temperatures as ethanol concentration is increased. Although all responses exhibited evidences of interactions between parameters, as shown in
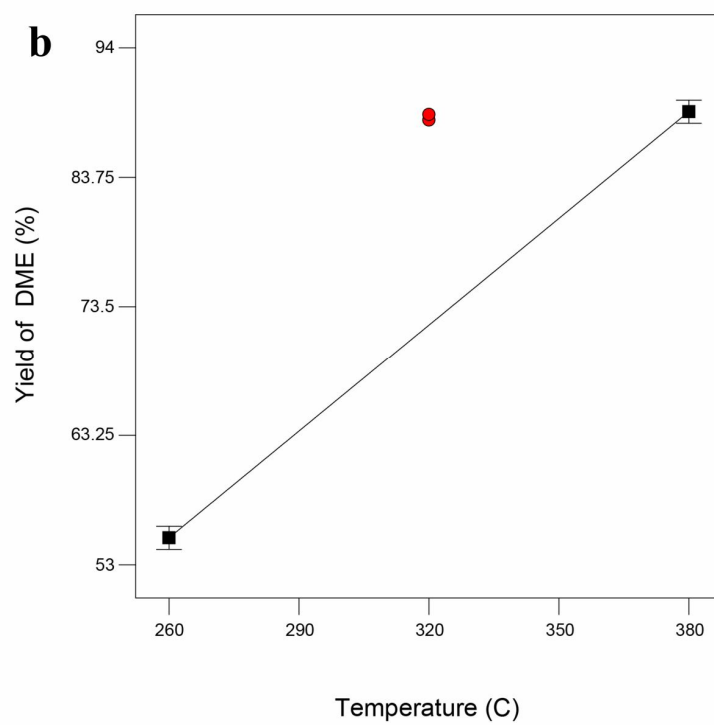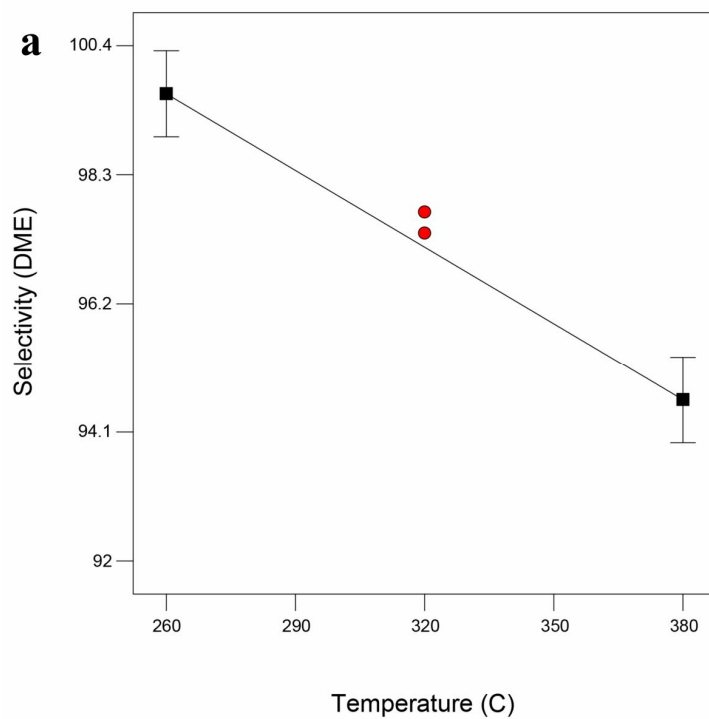
Fig. 2. Effects of temperature on (**a**) DME selectivity (**b**) Yield of DME (**c**) conversion to DME (**d**) yield of hydrocarbons and DME.
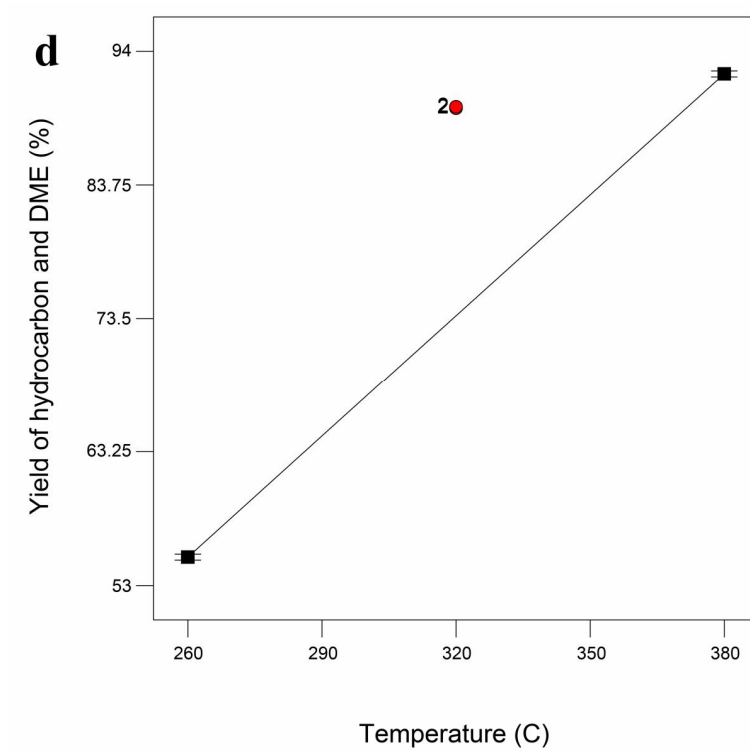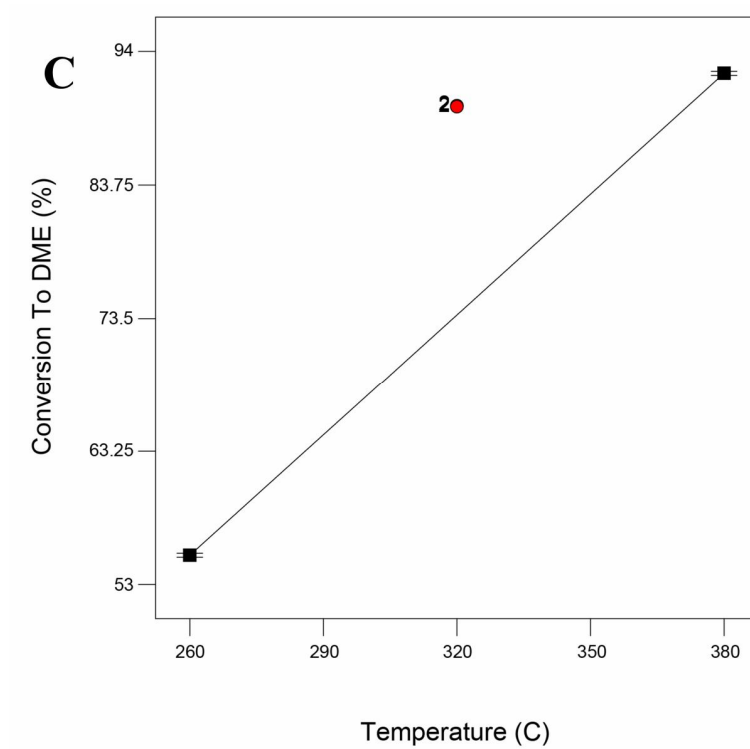
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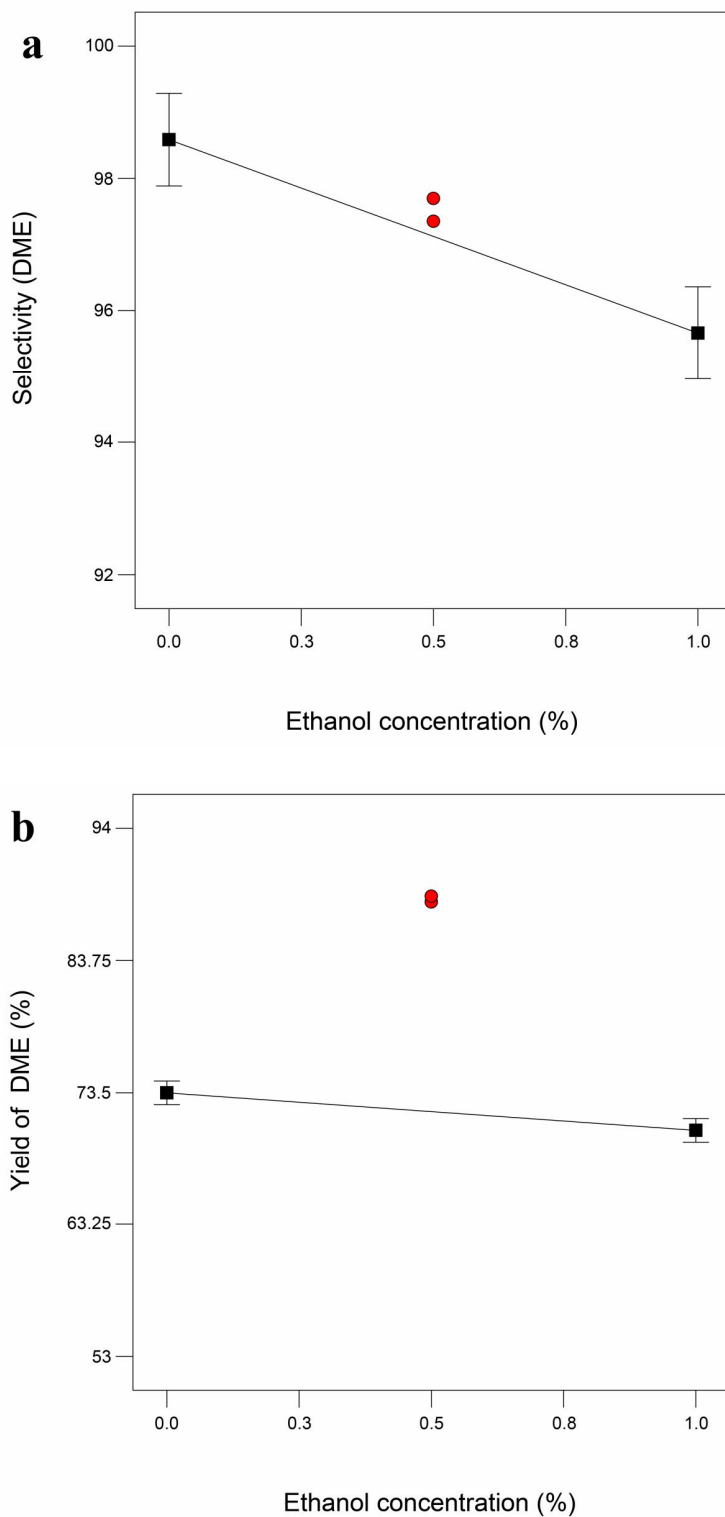
a

b

Fig. 3. Effects of the ethanol concentration on (**a**) DME selectivity (**b**) Yield of DME (**c**) conversion to DME (**d**) yield of hydrocarbons and DME.

c

Conversion To DME (%) vs Ethanol concentration (%)

d

Yield of hydrocarbon and DME (%) vs Ethanol concentration (%)

Fig. 3. Continued.

a

b

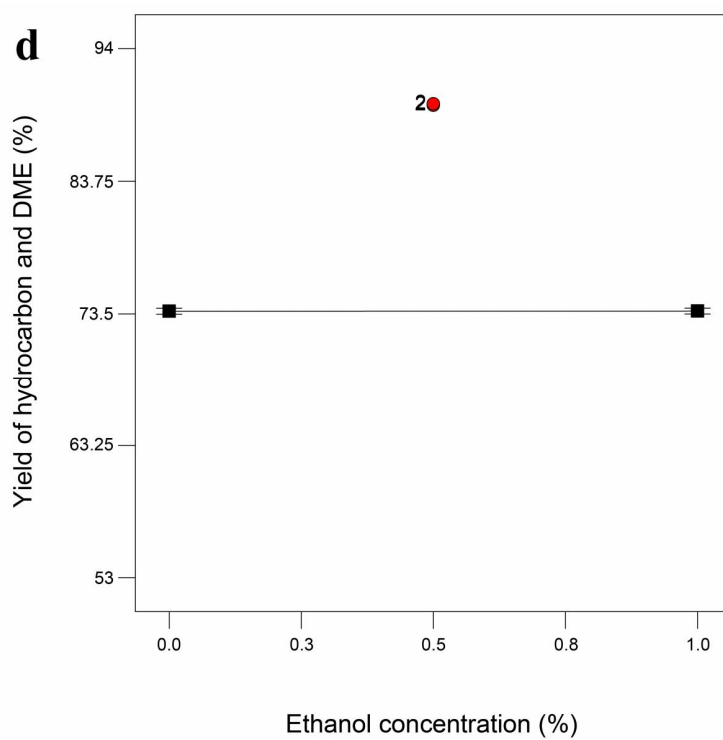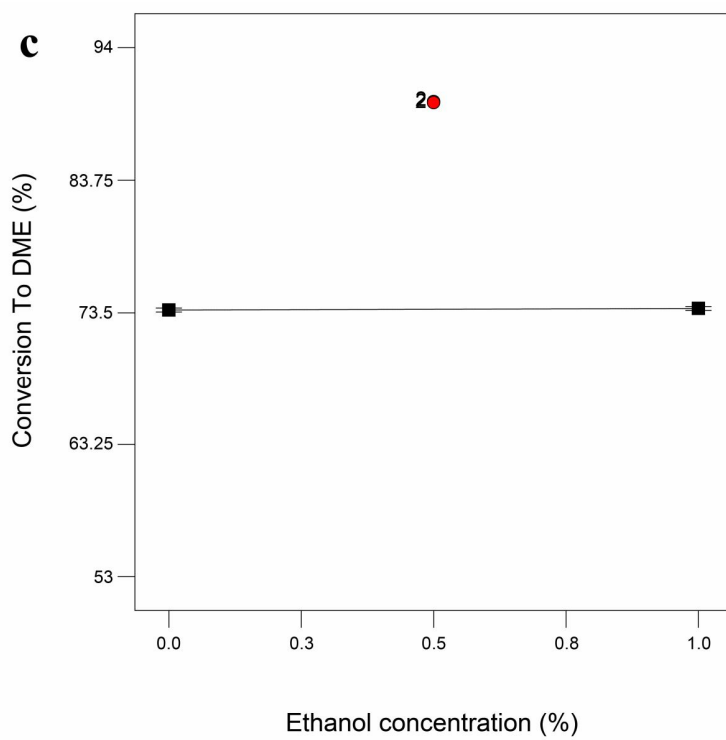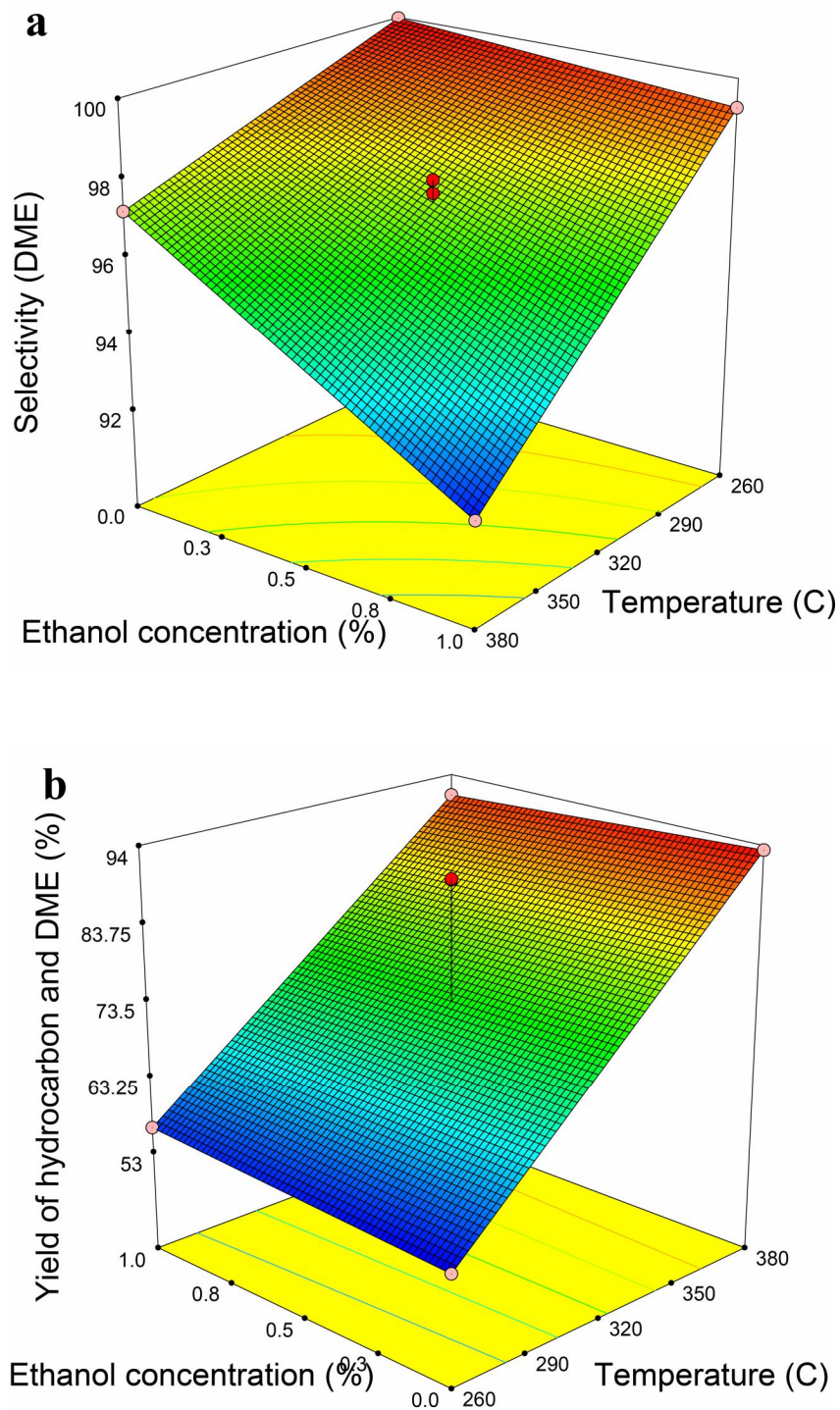**Fig. 4.** Simultaneous effects of two parameters (ethanol concentration and temperature) on (**a**) DME selectivity (**b**) yield of hydrocarbons and DME (**c**) yield of DME.
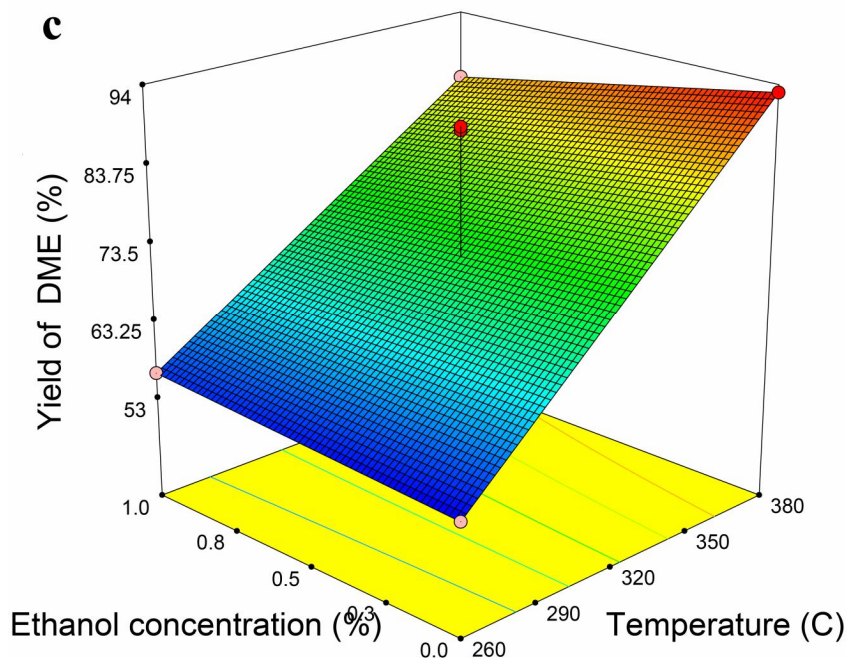
Fig. 4. Continued.

Fig. 4, the interactions were more remarkable in Fig. 4b, because ethanol concentration did not impose any significant effect on the yield of hydrocarbons and DME, singly, according to Fig. 3. This confirmed the capability of statistical analysis and DOE approach compared to the traditional (one-factor-at-a-time) strategy.

Analysis of Variance (ANOVA)

Table 4 presents the ANOVA results. According to ANOVA, values of "Prob > F" less than 0.05 and 0.1 indicate that the model and its terms are significant at 95% and 90% confidence interval, respectively.

Values greater than 0.1, however, indicate insignificance of the model terms. Hence, temperature (A), and temperature-ethanol concentration interaction (AB) were found to be of significant effects on all responses. Ethanol concentration (B) imposed significant effects only on DME selectivity, and yield of DME. These results were confirmed by the surface analysis whose results are shown in Figure 4. Curvature is measured as the difference between average value of a given variable at the center points and that at the factorial points. As shown in Table 4, only DME selectivity was of insignificant P-value. Indeed, the "curvature p-value"

of 0.308 implied that the curvature in the design space was not significant relative to the noise. Consequently, six experiments based on a 2^2 level factorial design with two center points were sufficient for describing a model for predicting DME selectivity. The empirical model in terms of the coded factors is as follows:

$$Selectivity = 97.12 - 2.5A - 1.46B - 1.1AB \qquad (7)$$

The model p-value of 0.05 implied that the model was significant. In addition, the model accuracy was confirmed by R-Squared (0.9985) and Adj. R-Squared (0.9938) values are close to 1 and also an adequate precision value (35.661) is greater than 4.

This model shows that all three parameters have negative effects on the DME selectivity. It is in agreement with previous results presented in the Section 3.1 (Figs. 2a, 3a and 4a).

Catalyst Characterization

Characterization of both fresh and tested gamma alumina catalysts was carried out using BET surface area measurements as well as scanning electron microscopy

Table 4. Analysis of Variance (ANOVA) for the Responses

Source	p-value			
	DME selectivity	Conversion to DME	Yield of DME	Yield of hydrocarbon & DME
Model	0.05 significant	0.0019 significant	0.0118 significant	0.0027 significant
Temperature (A)	0.031	0.0009	0.0060	0.0014
Ethanol (B)	0.0528	0.2706	0.0693	0.9144
Interaction (AB)	0.07	0.0145	0.0387	0.0213
Curvature	0.308 not significant	0.0019 significant	0.0106 significant	0.0027 significant

Table 5. BET Results for Both Fresh and Tested γ-Al$_2$O$_3$ Catalyst Showing the Occupation of Catalyst Active Sites by Ethanol and Hydrocarbons

Catalyst	Specific surface area (m^2 g^{-1})	
	Fresh catalyst	Tested catalyst
γ-Al$_2$O$_3$	158.8215	122.5649

Table 6. Comparison between the Results of Selectivity Model and Experimental Data

Run	Temperature ©	Ethanol con.	Experimental	Model
1	320	0.0	99.970	97.880
2	260	0.5	99.619	99.620
3	380	0.5	93.863	94.620
4	320	1.0	95.401	93.860

techniques. According to the BET results (Table 5), specific surface area of the used catalyst was lower that of the fresh one due to the coking phenomenon.

SEM observations (Fig. 5) further showed the differences in morphology between fresh and tested catalysts, indicating occupation of catalyst active sites on
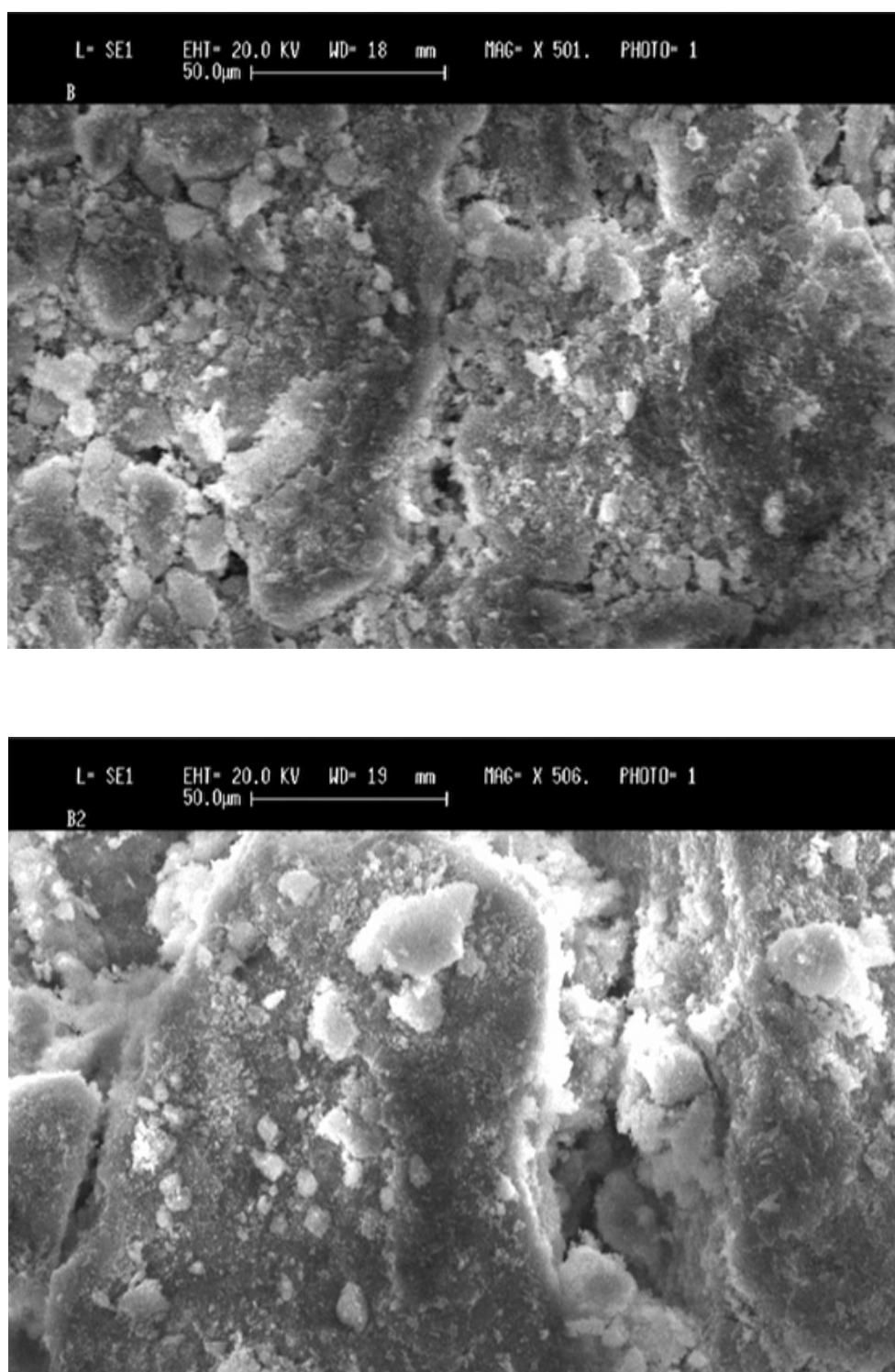
Fig. 5. SEM image of (a) fresh γ-Al$_2$O$_3$ catalyst (b) tested γ-Al$_2$O$_3$ catalyst (deactivated by coking).

the catalyst by ethanol and hydrocarbons.

Conformation Test

The selectivity model was validated using new experimental data; the corresponding comparison is reported in Table 6.

The comparison indicates that the calculated results were not significantly different from the experimental data. However, the observed difference at lower temperatures was lower than that at higher temperatures. Further observable in Table 6 is the negative effect of temperature on the model. Therefore, the suggested empirical model for the prediction of DME selectivity was proved to be valid and significant, demonstrating the capability of the two-level full factorial design for the interpretation of the experimental data and that of the proposed empirical modeling in the methanol dehydration reaction.

CONCLUSIONS

Dimethyl ether is a valuable chemical which can serve as a clean alternative to fossil fuels. Along the indirect approach to industrial DME production, methanol feedstock usually contains a few percentages of ethanol. Hence, in the present paper, the effects of ethanol concentration were investigated at different temperatures, using a two-level factorial design with two center points. The results showed that an increase in temperature led to decreased DME selectivity while increasing the yield of DME, the yield of hydrocarbon/DME and methanol conversion. In addition, an increase in ethanol concentration was observed to decrease the selectivity and yield of DME, even though it was associated with no significant effect on methanol conversion and yield of hydrocarbon production. Studied parameters (temperature and ethanol concentration) simultaneously showed that their interactions had a significant effect on the yield of hydrocarbon/DME production. Applying the DOE-derived experimental data, a selectivity model was developed following a statistical regression-based approach. The model was subsequently validated using the experimental data, with its accuracy demonstrated using ANOVA. In conclusion, for DME selectivity with no

significant curvature in ANOVA, the two-level factorial design of experiment was found to be a promising method for modeling and interpretation of experimental data, because of the low number of experiments it requires and large capabilities it offers.

ACKNOWLEDGEMENTS

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