

Mathematical modeling for ethanol conversion using transition metal (Fe, Co, Cu, and Ag) modified FSM-16 catalysts

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Abstract

FSM-16 silica mesoporous material was synthesized and modified by impregnation with iron, cobalt, copper, and silver. Catalytic dehydration and dehydrogenation of ethanol into ethylene and acetaldehyde were used as model reactions. The mathematical expressions for the formation of ethylene and acetaldehyde compounds were estimated for the investigated catalysts. Factorial design of two factors (metal percent, 3-9 wt. %, and reaction temperature, 250-450°C) was switched on. The significance of the regression coefficients and the adequacy of the equation were tested on the basis of the student *t* – test and Fisher's test (*F*). Both, the values of metals loading and temperature should be increased to increase the ethylene formation regardless of the Fe/FSM-16 catalyst. However the metal loading (positive or negative), is the most influential factor for the acetaldehyde formation except with Cu/FSM-16 catalyst. Such study helps in choosing the appropriate catalysts and conditions for petrochemical industry.

Keywords: Mathematical modeling; Ethanol conversion; Mesoporous material; Transition metal catalysts

1. Introduction

FSM-16 is a mesoporous silicate with a higher thermal and hydrothermal stability than MCM-41. It has a high surface area and a large pore volume with highly ordered hexagonal packed cylindrical pores [1, 2].

Alcohol conversion considered as a model test reaction of acid–base/redox properties of many catalysts. Meanwhile, such reactions produce a variety of products that have a vital industrial importance [3].

The dehydrogenation of saturated hydrocarbons to alkenes, which is used as an intermediate in the production of new fuels and fuel additives, has gained more importance in chemical industry in the past several decades.

Ethanol dehydration/dehydrogenation into ethylene and acetaldehyde was investigated using different transition metal catalysts such as silver / silica gel catalysts prepared by chemical reduction method [4], Fe ion-exchanged mordenite [5], copper catalysts on rice husk ash prepared by incipient wetness impregnation [6], cobalt-based catalysts used for high efficiency steam reforming of ethanol [7].

Alcohols dehydrogenation products (aldehydes and ketones) are preferentially formed on basic catalysts, while the dehydration products (olefins and ethers) are favored when acidic sites are present [8, 9, 10]. With regard to the reaction mechanism, one of the widely accepted mechanisms of alcohols conversion over metal oxides: (i) adsorption and activation of the alcohol on active metal site, and (ii) decomposition of the alkoxide intermediate to form the reaction products.

Mathematical modeling is more practical than kinetics since it mathematically configured the reaction regardless of knowing its mechanism which is difficult to know in many reactions in case of kinetic studies. Thus mathematical modeling does not take in account the intermediate steps of reactions and consider it as black box.

2. Experimental

2.1. Catalysts preparation

The parent silica FSM-16 material (Folded Sheet mesoporous material) was synthesized by a standard procedure described elsewhere [11]. This sample with surface area = $931 \text{ m}^2\text{g}^{-1}$ and BJH pore diameter of 2.5 nm was used as a support for the prepared catalysts.

The Fe, Co, Cu, and Ag oxide catalysts were prepared from the corresponding nitrate precursor. A predetermined amount of the precursor solution was added gradually with stirring to a crystallizing dish containing a predetermined amount of the support to make the specified weight percent, namely, 3, 6 & 9 of the metals on the FSM-16. The contents were continuously stirred while excess distilled water was evaporated. A thick paste was obtained that was dried in an oven at 110°C overnight. The catalyst powder was calcined at 250°C (temp.ramp $5^\circ\text{C}/\text{min}$.) in air for four hours. After that the supported metal oxide samples were heated in H_2 atmosphere for 4 h at 450°C . Characterizations of these catalysts was studied carefully in other papers.

2.2. Catalytic activity

The catalytic activity of the investigated catalysts was tested through the dehydration and dehydrogenation of ethanol by using a micro catalytic pulse technique. Ethanol was injected in micro quantities ($2\mu\text{L}$) by micro syringe in the form of pulses into a micro reactor containing 0.25 gm of the tested catalysts. The catalyst bed was supported on fine quartz wool and an inert glass placed at the top of this bed. The reactor effluent was passed through a chromatographic column for separation and determination using flame ionization detector. Computerized data acquisition system was used for integrating and recording the effluent yield. The column used 200 cm length and 0.3 cm diameter, packed with acid washed chromosorb AW (80–100 mesh size) from Merck, loaded with 15% by weight squalane (Merck). The reactions were carried out under atmospheric pressure in the temperature range $250\text{--}450^\circ\text{C}$ with 50°C interval. The hydrogen flow rate was kept constant at 50 mL per minute. Prior to catalytic activity test, the catalyst samples were heated in flowing H_2 up to 450°C with a heating rate of $100^\circ\text{C}/\text{h}$ and kept for 2h at 450°C for their activation. Few doses of ethanol were injected first to reach steady state of the activity. The chromatographic column temperature was adjusted and controlled at 70°C . The reaction products were ethylene, acetaldehyde together with diethylether.

3. Results and discussion

The mathematical modeling of the results was followed up in the experimental activity yield (Y) using different catalysts. The aim of this work was to evaluate the influence of both metal loading X_1 (3–9%) and temperature X_2 ($300\text{--}400^\circ\text{C}$) on the activity through two reactions: [reaction A] ethanol dehydration to ethylene and [Reaction B] ethanol dehydrogenation to acetaldehyde, hence; an optimum direction of the experiment could be achieved.

In our case as we examine only two factors, a full factorial design was switched on, in which the number of combination (N) = n^k [12], where k is the number of factors and n is the number of level. For simplicity purpose, we closed, in addition to the center point of design, two levels (two values of the independent variables). The coded design can be portrayed as shown in Fig.1

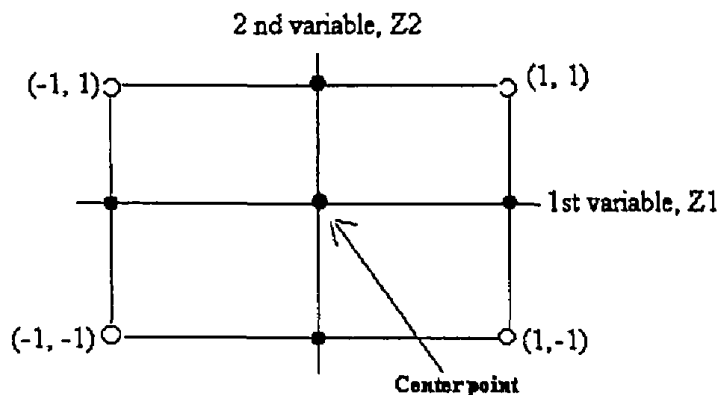


Fig. 1: Graphical representation of 2² design

The positive unity indicates the maximum value or the upper level of the factor value, while the negative unity expresses the lower value.

The coordinates of the center point is given by the equation:

$$X_1^0 = (X_{1_{\max}} + X_{1_{\min}}) / 2$$

The interval of variation between values of any-factor can be gained by:

$$\Delta X = (X_{1_{\max}} - X_{1_{\min}}) / 2$$

It is usual to pass from X₁, X₂...X_k coordinates to a new dimensionless system of coordinates Z₁, Z₂...Z_k through the coded equation:

$$Z_j = (X_j - X_j^0) / \Delta X_j$$

It is easy to prove that the upper and lower limits of any factor will be coded 1 and -1, respectively. This is quite clear in Fig.1.

For example let us consider the case of using Co/FSM-16 catalyst in [Reaction A]. The experiment design could be tabulated as illustrated in Table 1:

Table 1: 2² experimental design

	Factors on natural scale		Coded factors		Y
	Metal (X ₁)	Temp.°C (X ₂)	Z ₁	Z ₂	
1	3 %	300	-1	-1	24.1
2	9 %	300	+1	-1	32.3
3	3 %	400	-1	+1	54
4	9 %	400	+1	+1	52.7

For X_1 : $X_1^0 = 6\%$; $\Delta X_1 = 3\%$ and for X_2 : $X_2^0 = 350^\circ\text{C}$; $\Delta X_2 = 50^\circ\text{C}$

As we have two independent variables the resulted mathematical expression will have the form:

$$Y = \beta_0 + \beta_1 Z_1 + \beta_2 Z_2 \quad (1)$$

Or
$$Y = \beta_0 + \beta_1(X_1 - 6) / 3 + \beta_2(X_2 - 350) / 50 \quad (2)$$

The constants of the equation, i.e., β_0 , β_1 and β_2 are calculated according to the following system of equation

$$\beta_0 = \sum_{i=1}^n Z_{0i} Y_i / n, \quad \beta_1 = \sum_{i=1}^n Z_{1i} Y_i / n \quad \& \quad \beta_2 = \sum_{i=1}^n Z_{2i} Y_i / n \quad (3)$$

To realize these computations in a simple manner, table 2 was prepared:

Table 2: Calculation procedure of fitting process

N	Z_0	Z_1	Z_2	$Y_{(A)}$	$Z_0 Y$	$Z_1 Y$	$Z_2 Y$
1	1	- 1	- 1	24.1	24.1	- 24.1	- 24.1
2	1	+ 1	- 1	32.3	32.3	32.3	- 32.3
3	1	- 1	+ 1	54	54	-54	54
4	1	+1	+ 1	52.7	52.7	52.7	52.7
Σ					163.1	6.9	50.3

According to the system of equation (3), we get $\beta_0 = 40.775$, $\beta_1 = 1.725$ and $\beta_2 = 12.575$. Then the equation of [Reaction A] using *Co/FSM-16 catalyst* that describes the activity from equation (1) is given by:

$$Y = 40.775 + 1.725 Z_1 + 12.575 Z_2$$

This equation as we know represents the coded independent variables, but if we are in need to have the exact equation that concludes the real factors equation (2), we get the following multiple regression equations:

$$Y = 40.775 + 1.725 (X_1 - 6) / 3 + 12.575 (X_2 - 350) / 50$$

In running some arithmetic operations we get:

$$Y_A = - 50.7 + 0.575 X_1 + 0.252 X_2 \quad [\text{for Reaction A}]$$

and
$$Y_B = 11.75 + 0.892 X_1 - 0.019 X_2 \quad [\text{for Reaction B}] \quad (I)$$

Following up the same procedures for each of the used catalysts in both reactions, we get the following equations (experiment design is shown in table 3).

For Fe/FSM-16 catalyst:

$$[\text{Reaction A}]: Y_A = - 65.45 - 0.458 X_1 + 0.282 X_2$$

$$[\text{Reaction B}]: Y_B = 12.25 - 0.375 X_1 + 0.0035 X_2 \quad (II)$$

For Ag/FSM-16 catalyst:

$$[\text{Reaction A}]: Y_A = -76.05 + 1.675 X_1 + 0.286 X_2$$

$$[\text{Reaction B}]: Y_B = 26.4 - 1.392 X_1 - 0.0075 X_2 \quad (\text{III})$$

For Cu/FSM-16 catalyst:

$$[\text{Reaction A}]: Y_A = -56.9 + 1.2 X_1 + 0.224 X_2$$

$$[\text{Reaction B}]: Y_B = -6.9 + 0.075 X_1 + 0.091 X_2$$

Table 3: The overall experimental design of catalytic activity for both reactions A & B using different catalysts and considering two factors: Metal loading & Temperature through a 2² design

Metal % (X ₂)	Temp. °C (X ₁)	Co/FSM-16		Fe/FSM-16		Ag/FSM-16		Cu/FSM-16	
		[A]	[B]	[A]	[B]	[A]	[B]	[A]	[B]
-1	-1	24.1	7.8	16.1	11	14	19.2	13.6	18.5
-1	+1	54	8.1	47.3	13.7	43.8	20	36.8	31.5
+1	-1	32.3	15.3	16.4	11.1	25.3	12.4	21.8	22.9
+1	+1	52.7	11.3	41.5	9.1	52.6	10.1	43.4	28

In seeking for the influence of each independent variable whether it is positive or negative we design a table that considers only the direction of influence. This table summarizes and indicates a lot of information.

Table 4: Output of sensitivity analysis

Catalyst	Reaction A		Reaction B	
	Metal % (X ₁)	Temp. °C (X ₂)	Metal % (X ₁)	Temp. °C (X ₂)
Co/FSM-16	⊕	+	⊕	-
Fe/FSM-16	⊖	+	⊖	+
Ag/FSM-16	⊕	+	⊖	-
Cu/FSM-16	⊕	+	+	+

The circles indicate stronger influence; sign indicate the direction of influence. The positive sign is evidence that both the dependent variable (Y) and the independent one (X) are varying in the same direction. The opposite is the case with negative sign.

As seen from Table 4, in Reaction (A) almost the influence of both metal loading and temperature is positive, i.e., the values of both factors should be increased to increase the activity toward dehydration of ethanol. Investigating the independent factors we get that the stronger influence always belongs to metal loading, so, special attention is to be devoted to its variability. Exceptional situation is in case of Fe/FSM-16 catalyst where activity increase with decrease of iron loading (-ve).

But in case of Reaction (B), increasing or decreasing the metal loading (positive or negative), is the most influential factor rather than temperature for the ethanol dehydrogenation to acetaldehyde

regardless Cu/FSM-16 catalyst (see equation I, II& III). For both A and B reactions, metal loading has stronger effect than temperature whatever in + ve or - ve direction.

By making replicate observation, it was possible to determine S_e^2 , to test the significance of the regression coefficients, and, by considering that the degrees of freedom, also the adequacy of the equation is obtained. The significance of each coefficient can be tested on the basis of the student t -test [13]. Deletion of insignificant coefficient from the regression equation will have no effect on the remaining coefficients.

For example, [Reaction A] in the presence of Co/FSM-16, three replicate observations have been made at the center of the design (at 6% metal and 350°C) to yield the following values: $Y_1^0 = 23.9$, $Y_2^0 = 22.4$ and $Y_3^0 = 21.2$.

Hence

$$\bar{Y}^0 = 1/3 \sum_{u=1}^3 \bar{Y}_u^0 = 22.5$$

$$S_e^2 = 1/2 \sum_{u=1}^3 (Y_u^0 - \bar{Y}^0)^2 = 1.83$$

$$S_e = \sqrt{S_e^2} = 1.353$$

All coefficients can be determined with the same accuracy

$$S_{b_j} = S_e / \sqrt{N} = 0.677 \quad \text{where } N = 4$$

The significance of coefficients can be tested, using the Student t -test:

$$t_j = B_j / S_{b_j} \quad \text{where } B_j: \text{ is the actual coefficient value}$$

$$t_1 = B_1 / S_{b_1} = 1.725 / 0.677 = 2.54 \quad \& \quad t_2 = B_2 / S_{b_2} = 12.575 / 0.677 = 18.575$$

For a significance level of $\alpha = 0.05$ and $V = 2$ degrees of freedom, the tabulated value of the Student t -distribution is $t_{\alpha}(V) = 4.3$. Thus, all coefficients of the resulted equations that are much lower than 4.3 are insignificant and they could be deleted from the equations, without affecting their adequacy.

Now the estimated regression equation is tested to see how it fits the observations by using Fisher's test [14]. The variance ratio F is calculated through the formula:

$$F = S_{res}^2 / S_e^2$$

$$S_{res}^2 = \sum (Y_{act} - Y_{calc})^2 / N - L$$

Where, L is the number of significant coefficients in the regression equation. In our case $L = 3$ and $S_{res}^2 = 22.564$,

$$F = 22.564 / 1.83 = 12.33$$

The tabulated value of Fisher's test for $\alpha = 0.05$, $V_1 = 1$ and $V_2 = 2$ is $F_{1-\alpha}(V_1, V_2) = 18.5$.

As $F < F_{1-\alpha}(V_1, V_2)$, the above estimated regression equation fits the experimental data adequately.

Following up the same procedures for each of the used catalysts in both reactions, we get the values of Student t -test and Fisher's test (F) which is summarized in Table 5.

Table 5: Statistical test for fitting accuracy

Catalyst	Reaction	S_e^2	S_{res}^2	$F = S_{res}^2 / S_e^2$	Student t -test		Sb_j
					t_1	t_2	
Co/FSM-16	(A)	1.83	22.564	12.33	2.54	18.575	0.677
	(B)	1.72	4.624	2.688	4.078	1.41*	0.656
Fe/FSM-16	(A)	1.443	9.304	6.448	2.29	23.439	0.6005
	(B)	0.375	5.529	14.744	3.676	0.572*	0.306
Ag/FSM-16	(A)	4.304	1.564	0.363	4.661	13.242	1.078
	(B)	2.424	2.404	0.992	5.359	0.481*	0.779
Cu/FSM-16	(A)	2.443	0.64	0.262	4.731	14.322	0.782
	(B)	1.324	15.604	11.785	0.391*	7.856	0.576

* Insignificant coefficient

Accordingly the F values for both reactions (A& B) for all catalysts are lower than the tabulated value (18.5), hence the obtained experimental data was adequately fit the mathematical models derived.

The insignificant t_2 values much less than tabulated value (4.3) assure that temperature has no effect on the reaction B for Co, Fe& Ag supported on FSM-16. For the reaction B in the presence of Cu/FSM-16 catalyst sample, t_1 indicate that loading has no effect. .

4. Conclusion

Mesoporous silicate FSM-16 with a higher thermal and hydrothermal stability was synthesized. It has a high surface area and a large pore volume with highly ordered hexagonal packed cylindrical pores. Mathematical modeling for ethylene and acetaldehyde formation from ethanol conversion using iron, cobalt, copper, and silver modified FSM-16 catalysts was achieved. Both, the values of metals loading and temperature should be increased to increase the olefin formation regardless of the Fe/FSM-16 catalyst. However the metal loading (positive or negative), is the most influential factor for the oxygenate formation except with the Cu/FSM-16 catalyst. The obtained mathematical models are adequate and in line with the catalytic activity of the prepared Co, Fe, Ag& Cu supported on FSM-16 catalysts. Such study helps in choosing the appropriate catalysts and conditions for petrochemical industry.

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6. References

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