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Statistical optimization for oxidation of ethyl benzene over Co-Mn/SBA-15 catalyst by Box-Behnken design

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Abstract−A series of cobalt and manganese catalysts supported on SBA-15 with different loading of Mn^{+2} and Co^{+2} were synthesized. These samples were characterized by SEM and XRD techniques. The catalytic activity of these samples was evaluated in the oxidation of ethylbenzene (EB) to produce acetophenone (AP) and benzoic acid (BA) in the liquid phase using tert-butylhydroperoxide (TBHP) as an oxidant. The effects of Co-Mn loading, TBHP : EB molar ratio and temperature on acetophenone and benzoic acid yields were studied by Box-Behnken experimental design to optimize the production of acetophenone and benzoic acid in liquid system.

Key words: Benzoic Acid, Acetophenone, SBA-15, Cobalt-manganese Catalyst, Box-Behnken Design

INTRODUCTION

The scrutiny of molecules confined in porous media is an important subject that for decades has attracted extensive experimental and theoretical research, and there is a large amount of literature dealing with these problems and some examples are given in reference [1].

Thus, the realizing of geometrical and spatial restriction effects demands the study of porous materials under conditions of confinement where the pore structure, surface properties, dimensionality and size, are well controlling the recent discovery of highly ordered SBA-15 mesoporous materials [2]. Mesoporous material based supported catalysts have been proven to be the most ideal catalysts due to high surface area, high porosity, high stability, large and uniform channel size [3,4]. It was found that the support's porosity modified and improved the catalytic properties through its effect on cobalt particle dispersion and reducibility [5,6]. Heterogeneous catalysts have many intrinsic advantages such as easy recovery and recycling of the catalyst as well as suitability for sequential processing [7]. In addition, the chemical and structure properties of the support influenced the catalytic activity and product selectivity of cobalt catalysts through their modifications on the reducibility and dispersion of cobalt or the formation of desired phases. Sometimes it might be more affordable to modify or change the support properties than to increase the number of active sites [8]. Recently, it has been shown that mesoporous silicas are promising supports for cobalt oxides and cobalt metal catalysts [9-11] .The large surface area of the mesoporous SBA-15 ensures higher metal dispersion at cobalt loading up to 20 wt% compared to the conventional SiO_2 [10]. Usually cobalt nitrate precursor is used, as it is relatively well investigated and is known not to produce strong interaction with the support during the impregnation and under mild calcination treatment [12]. Manganese oxides have presented considerable importance in many applications, such as molecular adsorption, ion-exchange, catalysis, electrochemistry and magnetism, because of the structural flexibility with novel chemical and physical properties [13,14]. Co-Mn mixed oxides have also been reported as catalysts and also used in the combustion of volatile organic compounds (VOC) [15].

The purpose of the present study is to investigate the use of mesoporous silica, SBA-15, as support for Co and Mn bimetallic catalysts for liquid phase selective oxidation of ethyl benzene. To our knowledge, the use of SBA-15 as support for bimetallic Co-Mn systems and their application to liquid phase selective oxidation of ethylbenzene have not been reported previously. Furthermore, it was stated that the catalytic selective oxidation efficiency of this process is dependent on numerous parameters such as cobalt and manganese loading over SBA-15, reaction temperature and TBHP : Ethyl benzene molar ratio and these parameters need to be carefully optimized.

Using a one-factor-at-a-time optimization method is an intricate approach to evaluating the effects of different variables on an experimental outcome. In addition, this method is time consuming, expensive and often leads to misinterpretation of results when interactions between different components are present. Another approach to exactly evaluating the impact of the variables on the oxidation process is to change all the factors simultaneously in a systematic manner. This approach is referred to as response surface methodology (RSM). RSM is a statistical technique which can address the present scenario under consideration [16-18], and it can be used to establish relationships between multiple independent variables and one or more dependent variables. Developing a first-degree polynomial model can be performed by using statistical experimental designs. Also RSM optimizes multiple variables by systematic variation of all variables in a well-designed experiment with a minimum number of experiments. The RSM optimization process involves the following steps: (1) performing statistically designed experiments; (2) estimating the coefficients of a mathematical model using regression analysis technique; and (3) predicting the response and checking the adequacy and accuracy of the models [16,17].

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In this study, the effects of temperature, cobalt and manganese loading and TBHP:Ethyl benzene molar ratio to produce acetophenone and benzoic acid from ethyl benzene over SBA-15 catalyst were investigated. Box-Behnken design was used to obtain the optimum values of variables and studying the interactions between variables. Analysis of variance (ANOVA) was used to investigate the effects of main factors and their interactions. A quadratic model was proposed for responses (yield of acetophenone and benzoic acid) as a function of temperature, Co and Mn loading and TBHP : EB molar ratio. Results were used to obtain the optimum conditions for producing high quality products.

EXPERIMENTAL

1. Materials

All materials were of commercial reagent grade. The ethyl benzene substrate and cobalt and manganese were obtained from cobalt chloride [$Co(Cl)_2 \cdot 6H_2O$] and manganese chloride [$Mn(Cl)_2 \cdot 4H_2O$] and tert-butylhydroperoxide (TBHP) 70% solution in water were purchased from Merck chemical company. SBA-15 was prepared using tetraethyl orthosilicate (TEOS, Aldrich Co.) as the silica source, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, average molecular weight=5800, BASF Co.) as the template and HCl as the pH controlling agent. Acetonitrile as the solvent was supplied from Merck Company and used without further purification.

2. Catalyst Preparation

2-1. Preparation of SBA-15

Mesoporous silica SBA-15 was synthesized according to a literature procedure [2].

In a typical synthesis, 4 g of block copolymer P123 was dissolved in 30 g distilled water and 120 ml aqueous acidic solution of 2 M HCl, which was stirred at 35 °C for 3 h to get a transparent solution. Then, 8.5 g of TEOS was added to the above solution under vigorous stirring. This gel was continuously stirred for 24 h and then the solid product was collected by ltration, washed with distilled water, and dried at 100 °C overnight in air. The resulting powder was calcined at 530 °C for 6 h to remove surfactant.

2-2. Preparation of the Cobalt Containing SBA-15 Catalysts (Co/SBA-15)

In the first, the Co/SBA-15 catalysts with 5, 10, 15, 20 and 25 wt% Co were prepared by impregnation method. In a typical synthesis, 1.0 g of calcined and outgassed SBA-15 was impregnated with an aqueous solution of the cobalt chloride precursor, using the needed concentration to achieve the desired Co content assuming total incorporation. The wet solid was then dried at 80 °C overnight under vacuum and calcined in air under static conditions at 530 °C for 6 h.

2-3. Preparation of the Cobalt-manganese Containing SBA-15 Catalysts (Co-Mn/SBA-15)

The Co/SBA-15 catalysts containing manganese with 1, 2, 4, and 5 wt% Mn were prepared by impregnation method. In a typical synthesis, 1.0 g of calcined and outgassed Co/SBA-15 was impregnated with an aqueous solution of the manganese chloride precursor, using the needed concentration to achieve the desired Mn content assuming total incorporation. The wet solid was then dried at 80 °C overnight under vacuum and calcined in air under static conditions at 530 °C for 6 h.

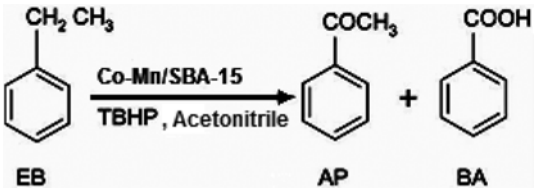

Fig. 1. Oxidation of ethylbenzene.

3. Catalyst Characterization

The structure of these samples was studied by X-ray diffraction (XRD) experiments. A Philips model PW 1800 diffractometer with Cu Kα radiation and Ni filter was used to collect the X-ray data. The scanning electron microscopy (SEM) images were obtained with a Philips XL30 instrument.

4. Experimental Design and Catalytic Reaction

We used the Box-Behnken design of experiment to find the optimal conditions for benzoic acid and acetophenone production. The effects of temperature (X_1), Co loading (X_2), Mn loading (X_3) and TBHP : EB molar ratio (X_4) were investigated, then the percentage of benzoic acid (y_1) and acetophenone (y_2) yield (%wt) were calculated in the final product.

Oxidation reactions of ethyl benzene were performed in a round bottom flask fitted with a water condenser using tert-butylhydroperoxide (TBHP, 70 wt%) as an oxidant.

A mixture of 0.2 g catalyst with the grain size of 200-230 mesh containing, 15 mL solvent (acetonitrile) and 30 mmol of ethylbenzene was stirred under nitrogen atmosphere at 50 °C for 30 min. The stirring rate of the solution was set at 750 cycle/min. Then TBHP was added to the solution and the mixture was heated at different temperatures (65-95 °C) under nitrogen atmosphere (Fig. 1). After reaction, the reaction mixture was cooled to room temperature. The products were analyzed by gas chromatograph GC (Perkin Elmer Model 8500) equipped with a flame ionization detector (FID) connected to a 3% OV-17 column with length of 2.5 m and diameter of 1/8 in.

5. Response Surface Exploration

Several preliminary tests were performed to evaluate the parameters' effect on oxidation of ethyl benzene over Co-Mn/SBA-15; temperature (X_1), Co loading (X_2), Mn loading (X_3) and TBHP:EB molar ratio (X_4) were regarded as the important factors. To investigate the optimum levels of those variables and to study their relationship, Box-Behnken experimental design was found to be more suitable. One of the advantages of Box-Behnken design (BBD) is that they are all spherical design; the sample combinations are processed such that they are located at midpoints of edges constituted by any two factors and require factors to be run at only of three levels that is represented by (−1, 0, 1) [19]. To minimize the number of variables, reaction time and amount of catalysts for the reaction were kept constant at 8 h and 0.2 g for all experiments, respectively. The effects of the temperature (X_1) Co loading (X_2), Mn loading (X_3) and TBHP : EB molar ratio (X_4) on %yield of the final product were studied.

The parameters should be normalized before analyzing the regression. The variables were coded as +1, −1 and 0 for three level, high, low and central, respectively. The actual variables (X_i) were coded

Table 1. Experimental range and levels for Box-Behnken design

Independent variables	Range and level		
	−1	0	1
Temperature (°C), X_1	75	85	95
Loading Co (wt%), X_2	5	15	25
Loading Mn (wt%), X_3	1	3	5
TBHP : EB molar ratio, X_4	1	2	3

by linear transformation is shown in the Eq. (1) as follows:

$$x_i = \frac{x_i - (X_{high} + X_{low})/2}{(X_{high} - X_{low})/2} \quad (1)$$

where x_i is the dimensionless coded value of ith factor, X_i is the uncoded value of the ith natural factor, X_{high} and X_{low} are the uncoded factor value at high and low level [20].

The three examined levels and experimental ranges of each independent variable are given in Table 1.

The relationship between the variables and the response was calculated by the second-order polynomial equation. The form of the full quadratic model is shown in the Eq. (2) as follows:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (2)$$

where Y is the predicted response or output (dependent variable), x_i and x_{ij} are the coded independent variables, β_0 is the intercept term, β_i the linear effect (first order), β_{ii} the squared effect, and β_{ij} is the interaction effect, i and j are the index numbers for variables.

Experimental design and data analysis were performed by using the statistical software SAS JMP, Version 8.0.2 [21].

RESULTS AND DISCUSSION

1. Catalysts Characterization

The low angle XRD patterns of SBA-15 (Fig. 2(a)) displayed two reflections; characteristics of the hexagonal structure and the more intense peak (1 0 0) revealed an interplanar distance of 9.7 nm and a cell parameter of 11.2 nm. Both Co/SBA-15 and Co-Mn/SBA-15 samples showed typical diffraction peaks, d_{100} reflection, associated to SBA-15 structure, indicating that the mesoporous support remained unchanged after metal impregnation and calcination steps, hence still retaining the ordered structure.

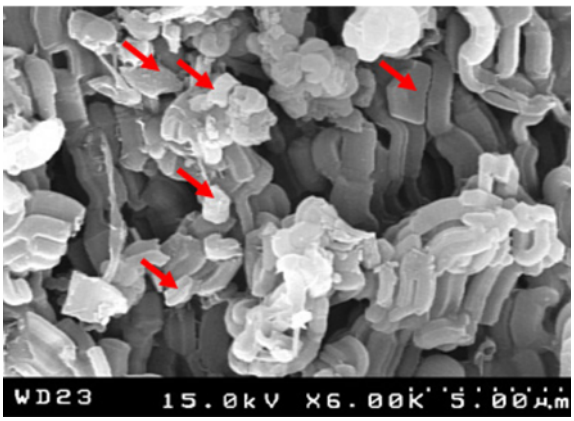

Fig. 3. SEM of Co-Mn /SBA-15. Particles with plate like shape indicated that agglomerated Co and Mn oxides.

The high angle XRD analysis of the Co-Mn/SBA-15 catalyst showed that the crystal phase of Co_3O_4 and $CoMn_2O_4$ deposited on the surface of SBA-15 and the average crystallite size determined from the diffraction peak broadening by using Scherer's formula was 7.7 nm (Fig. 2(b)). In addition, the SEM image (Fig. 3) of the catalyst indicated that agglomerated Co and Mn oxides particles were well deposited on the surface of SBA-15 and some of them were distributed within the SBA-15 mesoporous.

2. Analysis of Data and Development of the Response Surface Model

In the Box-Behnken design, 25-experimental observations were undertaken at random orders for the optimization of benzoic acid and acetophenone yields (y_1 and y_2 respectively) in the oxidation process. All experiments were carried out at atmospheric pressure for 8 h and amount of catalyst=0.2 g, then BA and AP yields were obtained. Table 2 shows the data resulting from the experiment of the effect of four variables, temperature (X_1), Co loading (X_2), Mn loading (X_3) and TBHP : EB molar ratio (X_4), where stirrer speed was kept unchanged at 750 rpm.

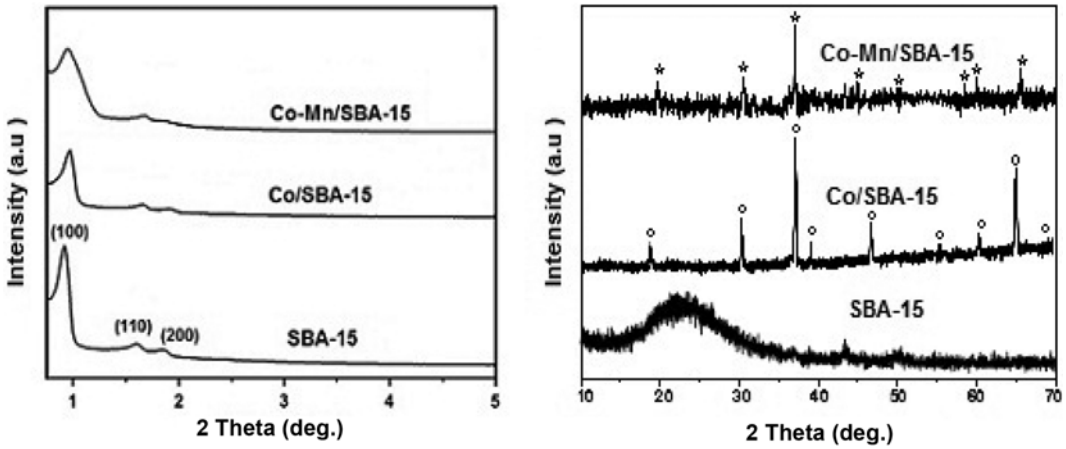

Fig. 2. X-ray diffraction patterns recorded for the SBA-15 support and mono/bimetallic Co-Mn /SBA-15. Phases identification: (°) Co_3O_4 (*) $CoMn_2O_4$.

Table 2. Experimental and Predicted of the benzoic acid and acetophenone yields

Run	T (°C)	Loading of Co (wt%)	Loading of Mn (wt%)	TBHP : EB	BA yield (wt%)		AP yield (wt%)	
	X_1	X_2	X_3	X_4	y_{1Exp}	y_{1Pred}	y_{2Pred}	y_{2Exp}
1	75	25	3	2	22.96	21.87	18.00	18.78
2	75	5	3	2	7.01	5.36	15.93	14.32
3	75	15	3	3	51.02	49.18	20.67	22.07
4	75	15	5	2	46.93	50.87	25.18	24.12
5	75	15	1	2	23.16	25.70	7.58	7.95
6	75	15	3	1	49.17	42.22	19.24	19.88
7	85	25	3	3	39.38	39.63	23.01	22.47
8	85	15	3	2	65.31	65.30	25.13	24.65
9	85	15	1	3	41.32	44.03	12.55	11.02
10	85	25	5	2	36.65	34.14	28.51	27.14
11	85	5	3	3	8.25	10.33	16.22	17.45
12	85	15	5	1	48.31	48.31	26.38	28.35
13	85	25	1	2	19.11	15.25	8.93	8.47
14	85	5	3	1	10.2	11.44	14.79	14.74
15	85	15	1	1	33.91	37.07	8.83	8.45
16	85	5	5	2	9.05	5.26	17.40	17.23
17	85	5	1	2	8.81	1.68	6.47	7.21
18	85	25	3	1	23.18	24.59	21.58	20.9
19	85	15	5	3	52.88	55.27	25.52	26.33
20	95	15	3	3	71.6	65.98	27.78	26.44
21	95	5	3	2	15.23	17.44	18.32	18.22
22	95	15	5	2	55.79	53.74	29.95	29.8
23	95	15	3	1	63.91	59.02	26.35	24.88
24	95	25	3	2	39.61	43.38	29.83	32.12
25	95	15	1	2	58.89	56.43	17.03	18.31

To investigate the effects of the main factors and their interactions, analysis of variance (ANOVA) was used. The stepwise regression method is to add variables in the earlier stage and eliminate unimportant variables subsequently. Backward elimination method was applied, and statistically insignificant terms (p>0.05) were deleted from the full quadratic model to obtain a final response surface model.

The model was refitted after successive elimination until an unsatisfactory fit occurred as indicated by a decrease in the adjusted R-square value. Backward elimination was adopted in this study since it is less probable to miss significant predictors that exhibit significant effect only in the presence of some other variables [22]. The results of the second-order response surface model fitting in the form ANOVA are given in Tables 3 and 4.

The F-value of 34.97 implies that the model is significant. In addition, the P>F of the model is less than 0.05, indicating that it is a significant and desirable model. The F test is defined as F=MSF/MSE, where MSF and MSE are the mean squares of factors or interactions, and errors, respectively. The P value of <0.0002 indicates that there is only a 0.02% chance that a model F-value this large is the product of noise in the experiments. The large value of F indicates that most of the variation in the response can be explained by the regression equation [23].

The equations indicate that BA and AP yields have linear and quadratic relationships with the four variables. Regression analysis revealed a coefficient of determination (R^2) value of 0.9798, indicating that the model does not explain only 2.02% of total variations. The adjusted determination coefficient ($AdjR^2$=0.9597) was also high, implying that the model has high significance. After the ANOVA test, it was observed that the factors X_1, X_2, X_3 and X_4 and interactions X_2^2, X_3^2, $X_1 \times X_3$, proved to be the statistically most significant effect on the yield of benzoic acid, and factors X_1, X_2,X_3 and interactions X_2^2, X_3^2, $X_1 \times X_2$ present statistically significant effects on the yield of acetophenone. A quadratic model with statistical significance from a combination of estimates for the variables and the ANOVA results can be produced. The quadratic model was used to explain the mathematical relationship between the independent variables and dependent responses as represented by Eqs. (3), (4).

$$y_1 = 65.310 + 7.898\,X_1 + 10.476\,X_2 + 4.784\,X_3 + 3.012\,X_4 + 3.357X_1X_2 - 6.968\,X_1X_3 + 2.825X_2X_3 + 4.442X_2X_4 - 5.492\,X_1^2 - 37.895\,X_2^2 - 12.176\,X_3^2 - 6.559\,X_4^2 \quad (3)$$

$$y_2 = 25.133 + 3.552\,X_1 + 3.393\,X_2 + 7.62\,X_3 + 0.715\,X_4 + 2.355\,X_1X_2 - 1.17\,X_1X_3 - 4.613\,X_2^2 + 2.17\,X_2X_3 - 5.194\,X_3^2 - 1.148\,X_3X_4 - 1.616\,X_4^2 \quad (4)$$

A positive sign before a term indicates a synergistic effect, while a negative sign indicates an antagonistic effect [24]. The presence of the significant XX cross terms in the model confirms that responses depend on both single and mixture variables. According to Eqs. (3) and (4) the binary terms indicate that there is a synergistic effect

Table 3. ANOVA of the model for the yield of BA from Box-Behnken

Source	Degree of freedom	Sum of square	F ratio	Prob>F
Model	14	9268.43	34.97	>0.0001
X_1 (75, 95)	4	1073.07	16.88	7.18E-05
X_2 (5, 25)	5	5527.84	69.59	1.93E-08
X_3 (1, 5)	4	919.41	14.46	0.0001
X_4 (1, 3)	3	309.32	6.490	0.0073
X_1X_2	1	45.091	2.83	0.1178
X_1X_3	1	194.18	12.22	0.0044
X_2X_3	1	31.92	2.00	0.1817
X_2X_4	1	78.94	4.96	0.0456
X_1^2	1	85.19	5.36	0.0390
X_2^2	1	4054.76	255.2	1.89E-09
X_3^3	1	418.64	26.35	0.0002
X_4^4	1	121.47	7.64	0.0171
Residual	13	509.08	22.31	.000
Lack of fit	3	25.40	1.05	0.350
Pure error	10	189.28		

R-Sq=97.98%; R-Sq (adj)=95.97%

Table 4. ANOVA of the model for the yield of AP from Box-Behnken

Source	Degree of freedom	Sum of square	F ratio	Prob>F
Model	14	1222.97	30.06	<.0001
X_1 (75, 95)	3	179.10	23.81	9.22E-06
X_2 (5, 25)	4	282.55	28.17	1.45E-06
X_3 (1, 5)	4	853.50	85.11	1.16E-09
X_4 (1, 3)	2	18.81	3.75	0.049584
X_1X_2	1	22.18	8.84	0.010043
X_1X_3	1	5.47	2.18	0.161585
X_2X_3	1	18.83	7.51	0.015924
X_3X_4	1	5.26	2.29	0.1537
X_2^2	1	103.35	41.22	1.6E-05
X_3^3	1	131.04	52.27	4.36E-06
X_4^2	1	12.67	5.05	0.041159
Residual	13	29.83	48.45	.000
Lack of fit	3	6.64	1.31	0.256
Pure error	10	29.7		

R-Sq=97.62%; R-Sq (adj)=95.60%

between Co loading (X_2) and two other variables (X_1 and X_3) for y_1 and y_2, whereas an antagonistic effect resulted between Mn loading and reaction temperatures.

Using data given in Table 2 the experimental yields of the benzoic acid and acetophenone (y_{exp}) versus predicted values (y_{Pred}) are plotted (Figures are not shown) and R^2 of the linear plot of benzoic acid and acetophenone was 0.978 and 0.980, respectively.

2-1. Effect of Process Variables on the Yield of Acetophenone and Benzoic Acid

The effect of the four factors on the responses variable is shown

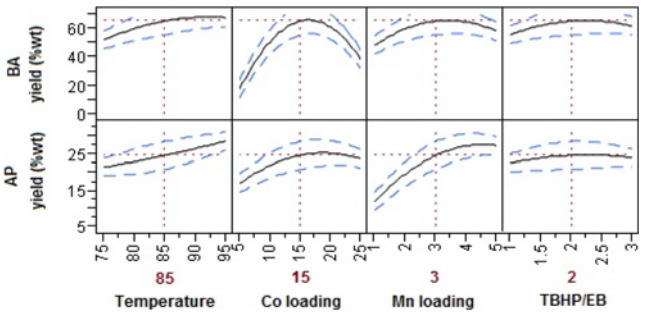

Fig. 4. Prediction profiler showing the influence of each variable on the responses; (*Top*: Benzoic acid yield, *Bottom*: Acetophenone yield).

in Fig. 4. In contrast to the traditional trial and error method, the prediction profiler provides an efficient way of changing one variable while keeping others constant to study the individual effects on the responses [25].

Main effects of factors (X_1, X_2, X_3 and X_4) on yield of BA and AP have been presented in Fig. 4. Reaction temperature plays an important role in the reaction progress. The yield of BA and AP is significantly increased with increase of temperature. An increase in TBHP : EB molar ratio will also increase both the yield of BA and AP, but only in the middle range. From Fig. 4, the yield of BA was increased by increasing the Co Loading (X_2) and then decreased in higher than 20% wt the Co loading. An increase in Mn loading, on the other hand, will increase yields but in range of higher than 3% will decrease yield of BA. As can be seen in Fig. 4, the yield of AP increased from 7.21% to 33.75% with Mn loading from 1 to 4.70 (%wt) and then became almost constant.

In the high range, the effect of Mn %wt is just opposite. When Mn %wt increases, yield of AP will increase because there are more active sites available for the reaction mechanism that leading to the production of AP while yield of BA will decrease in Fig. 4. Therefore, the prediction profilers are able to show the trend of the response resulting from the variation of one factor at a time. In the oxidation of ethyl benzene, the effect of individual process parameter on the yield of BA and AP was revealed and proved to be consistent with experimental results.

2-2. Contour Plots

Other than the individual effect contributed by each main variable, the responses were also influenced by the interaction variables. To gain a better understanding of the interaction effects of variables on yields, contour plots for the measured responses were formed based on the model equations (Eqs. (3), (4)).

Each response surface and contour plot was created by keeping two out of four variables constant at their center points. They can also be used for designing an optimum catalyst for the yield of benzoic acid and acetophenone vs. temperature, Co and Mn loading and TBHP : EB molar ratio. These plots are in Figs. 5 and 6. Note that only the contour profilers of significant interaction variables will be studied here because insignificant interaction variables do not result in much variation in the response within the factor region. In general, the shape of the contour plots is either straight, circular, elliptical or in the form of minimax [26]. If the shape of the contour is elliptical or inclined, the interaction between variables is evident

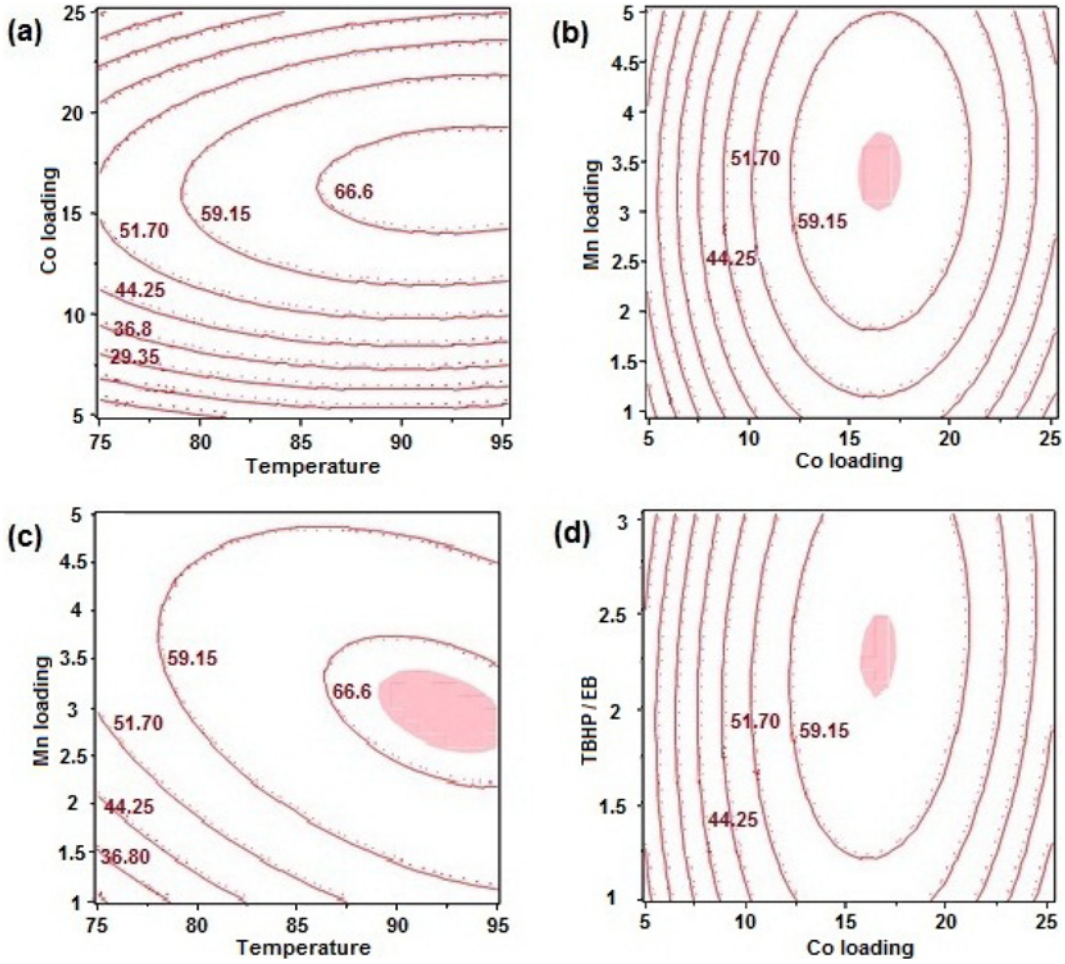

Fig. 5. Contours describing the response surface for BA as function of (a) Cobalt loading vs. Temperature at Mn loading=3 wt% and TBHP : EB molar ratio=2. (b) Manganese loading vs. Cobalt loading at Temperature=85 °C and TBHP:EB molar ratio=2. (c) Manganese loading vs. Temperature at Co loading=15 wt% and TBHP : EB molar ratio=2. (d) TBHP : EB molar ratio vs. Cobalt loading at Temperature=85 °C and Mn loading=3 wt%.

[25].

From Fig. 5(a), (c), at constant Co and Mn loading, the yield of benzoic acid is significantly increased with increase of temperature. In comparison, the contour plots in Fig. 5(b), (d) shows that maximum yield of BA at middle level of Mn loading and middle level of TBHP : EB was produced. The yield of BA decreased tom 51.70 wt% from 59.19 wt% by further increase of Mn and Co loading to 3.5 wt% and 20 wt%, respectively.

As mentioned, the yield of BA has an optimum amount with respect to Co and Mn loading, TBHP : EB molar ratio and temperature. At middle of Mn loadings, 16.90 wt% Co loading, TBHP : EB molar ratio=2.25 and 92.56 °C the yield of BA reached to a maximum amount, 69.70 wt% (Table 5).

Also, in these figures the third and fourth factors are held at the midpoint. The yield of AP increased slightly when temperature increased and reached a maximum. In Fig. 6(a), (c), at Co loading of 20 wt% and at Mn loading 4.5 wt% the increase of temperature resulted in increasing of AP yield and it reached to 28.98 wt%. Temperature had a different effect on the yields of BA and AP. At high temperature (95 °C) maximum yield of AP was observed while the optimum temperature for BA was 92.5 °C. Maximum yield of BA was obtained at moderate Co and Mn loading and high level of TBHP : EB, while high level of Co and Mn loading and low level of TBHP : EB maximized AP production. Fig. 6(d) shows the contour plot of X_3X_4, which is the interaction variable that remained after the backward elimination of the y_2 model. The red spots are the areas with the maximum yield. Notice that high yield correlated with middle of TBHP : EB levels.

Generally, the yield of BA and AP is significantly increased with simultaneous increase of temperature. This simply means that the %Mn and %Co loading are two factors which can be adjusted within the range to obtain a high conversion of benzoic acid and acetophenone.

2-3. Validation of the Experimental Model

Response optimizer helps to identify the combination of input variable settings that jointly optimize a single response or a set of responses [27]. The factor setting can be adjusted to get the initial solution. The values of the process variables for the maximum yield are shown in Table 5. The optimum values of the independent variables are obtained considering the initial and final values of temperature, cobalt loading, Mn loading and TBHP : EB molar ratio. A yield of higher than 28.98% for acetophenone could be achieved

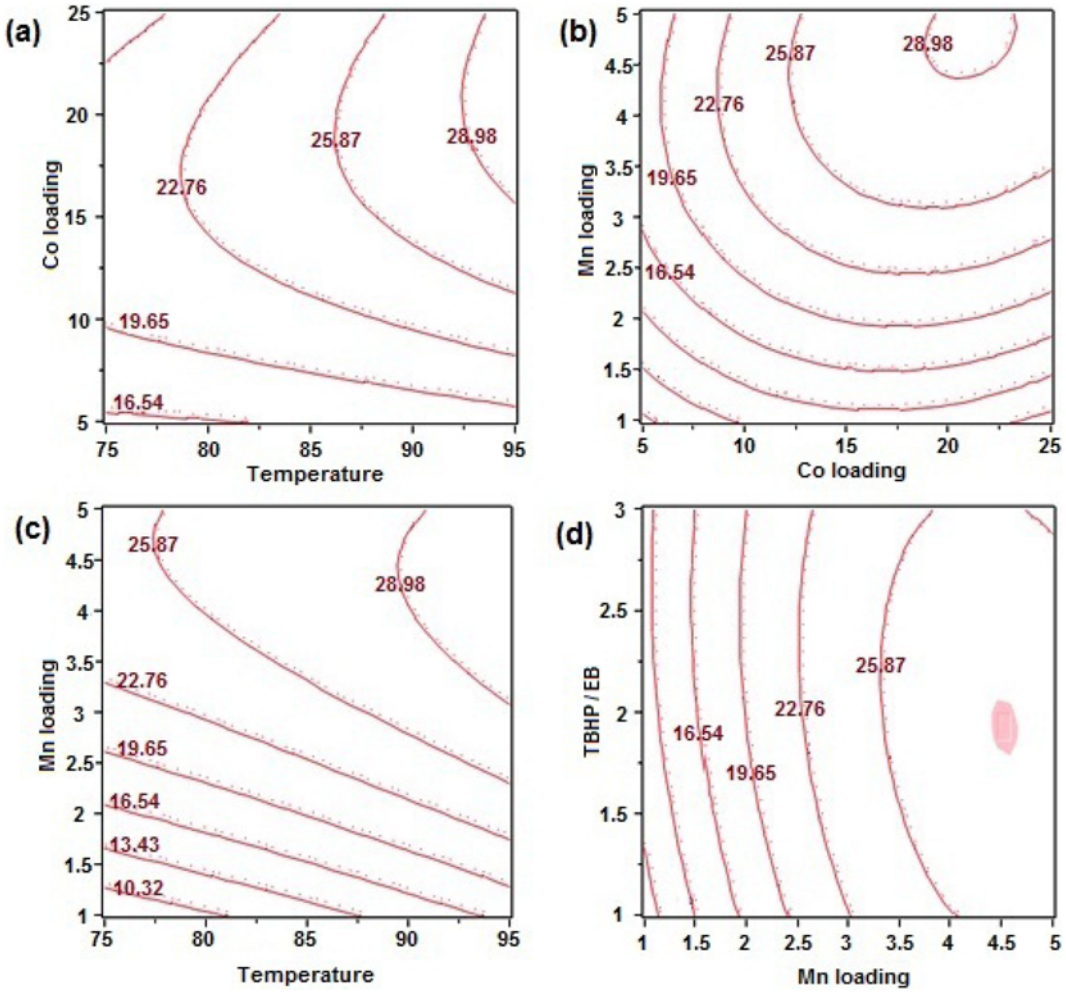

Fig. 6. Contours describing the response surface for AP as function of (a) Cobalt loading vs. Temperature at Mn loading=3 wt% and TBHP : EB molar ratio=2. (b) Manganese loading vs. Cobalt loading at Temperature=85 °C and TBHP : EB molar ratio=2. (c) Manganese loading vs. Temperature at Co loading=15 wt% and TBHP : EB molar ratio=2. (d) TBHP : EB molar ratio vs. Manganese loading at Temperature=85 °C and Co loading=15 wt%.

Table 5. Values of the process parameter for maximum yield of BA and AP

Temp. (°C) X_1	Co loading (wt%) X_2	Mn loading (wt%) X_3	TBHP : EB molar ratio X_4	Benzoic acid yield (wt%) y_1	Acetophenone yield (wt%) y_2
92.50	16.90	3.0	2.25	69.70	-----
95.00	23.65	4.70	1.95	-----	33.75

Composite desirability=1.00000

Table 6. Comparing the experimental and predicted values

Temp. (°C)	Co loading (wt%)	Mn loading (wt%)	TBHP : EB	Benzoic acid yield (wt%)		Acetophenone yield (wt%)	
				Experimental	Predicted	Experimental	Predicted
80	25	3	3	22.30	22.39	16.25	17.10
90	20	3	3	39.23	41.93	24.02	24.98
90	15	2	3	58.62	59.51	22.01	20.50
95	10	1	2	10.31	8.82	8.78	8.85

when using the cobalt loading higher than 20% (wt) and the manganese loading higher than 4% (wt) and the TBHP:EB ratio in the range of 1 to 2. The results found in Table 5 show the optimal values of the reaction conditions, on the basis of statistic analyses. The data and the response surfaces obtained allow suggesting the better operation conditions for this reaction in order to optimize the two responses

(y_1 and y_2 yield).

Also, to show the validity of predictions, using the prediction profiler, four data points with different values were randomly chosen to compare the experimental and predicted values so four more experiments were conducted and data are presented in Table 6. These results confirm that the predicted results satisfactorily match the experimental values. Thus the RSM was successfully applied to maximize the yield of BA and AP.

CONCLUSIONS

A response surface model, based on the Box-Behnken technique, was developed to describe the yield of benzoic acid and acetophenone production in liquid phase oxidation of ethyl benzene. The obtained results from ANOVA showed that the most significant factor affecting the yield of benzoic acid and acetophenone production was cobalt loading and manganese loading, respectively. In addition, the interactions between temperature and Mn loading ($X_1 \times X_3$), Co loading and temperature ($X_2 \times X_1$) had significant effects on the benzoic acid and acetophenone yield, respectively. Coefficient of determination (R^2) value of 0.9798 and 0.9762 obtained from Eqs. (3) and (4) shown that quadratic polynomial regression model could properly interpret the experimental data. At 92.50 °C and 16.9%wt of Co loading and middle level of Mn loading and TBHP : EB, we could achieve the highest yield of benzoic acid while at highest level of temperature and high level of Mn loading and 23.65% of cobalt loading and moderate values of TBHP : EB ratio the yield of acetophenone was maximized.

REFERENCES

1. C. Turner, J. Brennan, P. Johnson and K. Gubbins, *J. Chem. Phys. B*, **116**, 2138 (2002).
2. D. Zhao, J. Feng, Q. Huo, N. McIntosh, G. Fredrickson, B. Chmeika and G. Stucky, *Science*, **279**, 548 (1998).
3. S. S. Reddy, D. R. Burri, V. S. Kumar, A. H. Padmasri, S. Narayanan and K. S. Rama Rao, *Catal. Commun*., **8**, 261 (2007).
4. D. R. Burri, I. R. Shaikh, K. M. Choi and S. E. Park, *Catal. Commun*., **8**, 731 (2007).
5. R. Bechara, D. Balloy and D. Vanhove, *Appl. Catal. A: Gen*., **207**, 343 (2001).
6. D. Song and J. Li, *J. Mol. Catal. A: Chem*., **247**, 206 (2006).
7. S. B. Shrikant, S. Shylesh, K. R. Kamble and A. P. Singh, *J. Mol. Catal. A: Chem*., **255**, 123 (2006).
8. L. Jia, Litao Jia, D. Li, B. Hou, J. Wang and Y. Sun, *J. Solid State Chem*., **184**, 488 (2011).
9. E. V. Steen, G. S. Swell, R. A. Makhothe, C. Micklethwaite, H. Manstein, M. D. Lange and C. T. O'Connor, *J. Catal*., **162**, 220 (1996).
10. Y. Khodakov, V. L. Zholobenko, R. Bechara and D. Durand, *Micropor. Mesopor. Mater.*, **79**, 29 (2005).
11. Y. Khodakov, R. Bechara and A. Griboval-Constant, *Appl. Catal. A: Gen*., **254**, 273 (2003).
12. S. W. Ho, M. Houalla and D. M. Hercules, *J. Phys. Chem*., **94**, 6396 (1990).
13. J. Fei, Y. Cui, X. H. Yan, W. Qi, Y. Yang and J. B. Li, *Adv. Mater*., **20**, 452 (2008).
14. W. Xiao, J. S. Chen, Q. Lu and X. W. Lou, *J. Phys. Chem. C*, **114**, 12048 (2010).
15. J. J. Spivey, *Ind. Eng. Chem. Res*., **26**, 2165 (1987).
16. R. H. Myer and D. C. Montgomery, *Response surface methodology*, 2nd Ed., Wiley, New York, 343 (2002).
17. S. Ray, *Ind. Tex. J*., **117**, 24 (2006).
18. G. E. P. Box and N. R. Draper, *Empirical model building and response surfaces*, John Wiley & Sons Inc., New York, 477 (1987).
19. K. Yetilmezsoy, S. Demirel and R. J. Vanderbei, *J. Hazard. Mater*., **171**, 551 (2009).
20. D. Bas and I. H. Boyac, *J. Food Eng*., **78**, 836 (2007).
21. JMP, The statistical discovery software, user's guide, SAS, USA (2009).
22. G. Du, Y. Yang, W. Qiu, S. Lim, L. Pfefferle and G. L. Haller, *Appl. Catal. A: Gen*., **313**, 1 (2006).
23. P. Tripathi, V. Chandra Srivastava and A. Kumar, *Desalination*, **249**, 1273 (2009).
24. S. Y. Lu, J. Q. Qian, G. W. Zhang, D. Y. Wei, G. F. Wu, B. P. Yi, B. Pan and K. Y. Zhang, *J. Biochem. Technol*., **1**, 79 (2009).
25. Q. Tang, Y. Chen, C. Jasmine Zhou, T. Chen and Y. Yang, *Catal. Lett*., **128**, 210 (2009).
26. I. Istadi and N. A. Saidina Amin, *Fuel Process Technol*., **87**, 449 (2006).
27. N. Jose, S. Sengupta and J. K. Basu, *Fuel*, **90**, 626 (2011).