

Performance of nanostructure Fe-Ag-ZSM-5 catalysts for the catalytic oxidation of volatile organic compounds: Process optimization using response surface methodology

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Abstract—Gas phase catalytic oxidation of ethyl acetate was studied in low concentration over Fe-Ag-ZSM-5 catalysts under atmospheric pressure. The effect of important parameters such as Ag loading, Fe loading, calcinations temperature and reaction temperature was investigated and the process conditions were optimized using response surface methodology (RSM) based on central composite design (CCD). The optimum condition for Ag loading, Fe loading, calcination temperature and reaction temperature was 5.17 wt%, 2 wt%, 580 °C and 350 °C, respectively. A maximum of 96% of ethyl acetate was removed under the optimum experimental conditions. The proposed model equation using RSM has shown good agreement with the experimental data, with a correlation coefficient (R^2) of 0.949.

Key words: Catalytic Oxidation, VOC, Response Surface Methodology, Fe-Ag-ZSM-5, Ethyl Acetate

INTRODUCTION

Volatile organic compounds (VOCs) emitted in air during industrial processes using solvents, polymers and resins such as those involved in painting and coating operations [1,2] are considered as significant atmospheric pollutants producing harmful effects (toxicity, formation of O_3 , etc.) [1]. Environmental legislations fix restrictive standards on VOC emissions leading to the emergence of abatement technologies [3].

There are many techniques for controlling the emissions of VOCs. Among them, catalytic oxidation is an effective way for reducing the emissions of VOCs, due to its low energy requirement. In this way, two kinds of catalysts are usually applied: (i) noble metal based solids which possess high activity but are expensive, and (ii) metal oxides based samples which are cheaper but less active [4-7]. The choice between using a metal oxide or a noble metal to catalyze the VOC oxidation depends on several factors (nature of the stream to be treated, presence of contaminants, etc.) [8].

The choice of the support is also important. Furthermore, it is well known that supports play an important role in catalytic activity improvement, particularly in oxidation reaction [9]. The advantage of using a hydrophobic support is that moisture, both from the atmosphere and formed as a reaction product, will not adsorb on the catalyst, particularly at low reaction temperatures. Zeolites can also be used as supports or even as catalysts for oxidation reactions [10]. Zeolites are unique microporous crystalline materials having properties of thermal stability, shape selectivity, and resistance towards coke formation. Acidic and metal modified zeolites have found application as catalysts in petroleum refinery, production of fine chemicals and environmental catalysis [11].

The active components for the oxidation of VOC and chlorinated hydrocarbons are usually supported noble metals such as Pt, Pd and

Ag or the oxides of base metals such as cobalt, copper, manganese, vanadium, chromium, tungsten and mixtures of noble metals and metal oxides such as Cu-Co, Au-Fe, Cu-Ce, Pt-Ni, Pt-Sn on silica, alumina or zeolite [12-14]. One of the most significant advantages of precious metal catalysts for the removal of VOCs solvents is their ability to form complete combustion products. Lately, bimetallic catalysts have been given more attention in catalytic combustion applications. Most reports consider methane oxidation over Pd-Pt catalysts. The addition of Pt to a Pd catalyst has been shown to prolong the activity for methane combustion compared with monometallic Pd catalysts. Likewise, Pd-Ag has been reported to maintain its activity over time [15-17]. Narui et al. [18] attributed the superior combustion stability of Pd-Pt to higher dispersion of supported particles and suppression of particle growth. Factors which contribute to the catalytic properties of a bimetallic catalyst include: (a) the surface composition of the noble metal and (b) the strength of interaction between the noble metal and the catalyst support [19]. Silver has recently gained much interest for low temperature NO_x reduction [20] and CO oxidation [21]. Thus, it could be a suitable catalyst for many redox reactions like VOC oxidation. Pioneering works by Cordi and Falconer [22] led to the conclusion that Ag/ Al_2O_3 catalyst was very active for the complete oxidation of VOC to CO_2 and H_2O . VOC was hypothesized to diffuse along the alumina surface and reacted at the silver sites, where oxygen is adsorbed. As the oxidation occurred at high temperatures, VOC reacted in parallel on silver and alumina sites. Beak et al. [23] studied various transition metals such as Mn, Fe, Co, Ni, Cu, Zn and Ag over Y zeolite for catalytic oxidation of toluene and methyl ethyl ketone and silver showed the best activity among the tested catalysts.

RSM is one of the relevant multivariate techniques which can deal with multivariate experimental design strategy, statistical modeling and process optimization [24-29]. It is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors. This method is often employed after the vital controllable factors are identified and to

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find the factor settings that optimize the response. Designs of this type are usually chosen when a curvature in the response surface is suspected. The process optimization of the oxidation of VOC with the bi-metal catalyst has not been reported in literature. In our previous work [30], we have studied performance of interaction between Ag and Fe, Co, Mn in the complete oxidation of ethyl acetate. Since, Fe-Ag-ZSM-5 appeared to be the most active catalyst; hence the present work intends to assess the effects of variables such as Ag loading, Fe loading, calcinations temperature and reaction temperature to identify the optimum conditions for Fe-Ag-ZSM-5 catalyst in complete oxidation of VOCs, using a central composite design (CCD).

EXPERIMENTAL SECTION

1. Catalyst Preparation

The starting material was a NH_4 -ZSM-5 solid prepared by ion-exchange of Na-zeolite (from Iranian petroleum industry research center with a Si/Al ratio of 14) with NH_4Cl (1 M) by following the procedures previously reported [30]. The calcination led to the formation of H-form zeolites. Silver was introduced by a conventional ion exchange of the HZSM-5 zeolite. The zeolite was added to an aqueous solution of silver nitrate and the exchange was pursued for 24 h at 25 °C under stirring. After centrifugation the obtained solids were washed several times so as to remove non-exchanged ions. After drying overnight at 100 °C, the solids were calcined under an air flow at 500 °C for 5 h. In this paper these solids, prepared by impregnation, are named Ag-ZSM-5. Solids containing both Fe and Ag, which were prepared by successive impregnations with intermediate calcinations under O_2 at 500 °C, are named Fe-Ag-ZSM-5. Before the catalysts were used in the reactor, they were converted into pellets using a hydraulic pellet making press. The pellets were then crushed and sieved into particle sizes of between 200 and 250 μm . The particle size range was selected to limit the pressure drop across the catalyst bed as well as particle diffusion during the reaction.

2. Experimental Apparatus and Procedures

Catalytic combustion reactions of ethyl acetate were carried out under atmospheric pressure according to the procedure described in the literature [30]. The reactor consisted of a 0.8 cm i.d. U-shaped quartz tube placed in an electric furnace controlled by a proportional-integral-derivative controller (PID). Catalyst (0.2 g) was placed over a plug of quartz wool and a thermocouple was placed inside the catalyst bed. Before starting each run, zeolites were pre-treated with 10 mL/min of pure nitrogen at 200 °C in order to eliminate the possible compounds adsorbed on the zeolite surface. After this pre-treatment, the reactor was cooled to 100 °C, and the reaction vapor was introduced by passing the carrier gas (nitrogen) flow through a saturator containing the liquid ethyl acetate and the other air stream was used to maintain the molar concentration of ethyl acetate at about 0.2% in the full stream. The reactor was operated under excess oxygen condition and feed concentrations at gas hourly space velocity (GHSV) 30,000 h^{-1} . Measurements were taken from 150 to 450 °C; different temperatures were randomly tested in order to avoid variation of catalyst properties or hysteretic effects. The flow of gases was controlled by a needle valve (Parker Company). All experimental runs were taken under steady state conditions.

3. Experimental Design

Response surface methodology (RSM) is a collection of statisti-

cal and mathematical techniques useful for developing, improving, and optimizing processes [31,32]. By careful design and analysis of experiments, it seeks to relate a response, or output, variable to the levels of a number of predictor, or input, variables. The input variables are sometimes called independent variables, and the performance measure or quality characteristic is the response. The system involving a response Y that depends on the controllable input variables $\xi_1, \xi_2, \dots, \xi_q$. The relationship is

$$Y = h(\xi_1, \xi_2, \dots, \xi_q) + \varepsilon \quad (1)$$

where h is taken as the approximating response function and ε as a statistical error. If E denotes the expected values, then the mean value of ε is assumed to be zero, and the expected value of output variable is determined as follows:

$$E(Y) = \eta = E[h(\xi_1, \xi_2, \dots, \xi_q)] + E(\varepsilon) = h(\xi_1, \xi_2, \dots, \xi_q) \quad (2)$$

The variables $\xi_1, \xi_2, \dots, \xi_q$ in Eq. (2) are usually called the natural variables because they are expressed in the natural units of measurement. In much response surface methodology work it is convenient to transform the natural variables to the coded variables $X_1, X_2, \dots, X_p$, where these variables are usually defined to be dimensionless with mean zero and the same spread or standard deviation. In terms of the coded variables, the true response function is now written as

$$\eta = g(X_1, X_2, \dots, X_p; \beta) \quad (3)$$

Usually a low-order polynomial in some region of the independent variables space is appropriate. In many cases, the second-order model that includes the interaction term is required. It is widely used because of its flexibility. For the case of two variables, the second order model is suggested:

$$\eta = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (4)$$

This model would likely be useful as an approximation to the true response surface in a relatively small region. The method of least squares is employed for fitting empirical data to a regression function. In general, any regression model that is linear in the parameters (the values) is a linear regression model, regardless of the shape of the response surface that it generates.

Box and Wilson [32] gave the RSM to find the optimal response and the function relation between variables and response by the least experiments. When applying the RSM technique, the method of steepest ascent by making use of the first-order model is portrayed to explore a smaller region of interest or a region of initial experimentation before the application of the second order model. A central composite design (CCD) contains an imbedded factorial or fractional factorial design with center points that is augmented with a group of 'star points' that allow estimation of curvature. If the distance from the center of the design space to a factorial point is ± 1 unit for each factor, the distance from the center of the design space to a star point is $\pm \alpha$ with $|\alpha| > 1$. The precise value of α depends on certain properties desired for the design and on the number of factors involved.

If the assumption that interactions between more than two factors are negligible is correct, the CCD allows unbiased estimation of all main effects and two-factor interactions. Designs of resolution fine or more are of particular value as main building blocks of CCD which allows estimation of all the terms in a second degree

polynomial approximation.

In the present study, CCD which is a widely used form of RSM was employed for the optimization of catalytic oxidation of ethyl acetate by Fe-Ag-ZSM-5 catalysts. To evaluate the influence of operating parameters on the catalytic oxidation conversion of ethyl acetate, four main factors were chosen: Ag loading (wt%), Fe loading (wt%), calcination temperature (°C) and reaction temperature (°C). A total of 31 experiments were employed in this work, including seven replications at the center point. Experimental data were analyzed using the Minitab 14 software.

For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (6)$$

where X_0 is the value of X_i at the center point and δX presents the step change [33]. The experimental ranges and the levels of the independent variables for ethyl acetate oxidation are given in Table 1.

Table 1. Experimental ranges and levels of the independent test variables

Ranges and levels					Variables
+2	+1	0	-1	-2	
9	7	5	3	1	Ag loading (g) (X_1)
4.6	3.5	2.4	1.3	0.2	Fe loading (g) (X_2)
750	650	550	450	350	Calcination time (°C) (X_3)
400	325	250	175	100	Reaction time (°C) (X_4)

Preliminary experiments to determine the extreme values of the variables have been reported in our previous work [30].

RESULTS AND DISCUSSION

1. Model Results for Catalytic Oxidation of Ethyl Acetate

The following second-order polynomial response equation was

Table 2. Central composite design, experimental plan and results

Run	Ag loading (wt%)	Fe loading (wt%)	Calcination temperature (°C)	Reaction temperature (°C)	Oxidation conversion (%)	
					Exp. ^a	Pred. ^b
1	0	0	0	2	99	101
2	0	0	0	0	60.02	55.59
3	0	0	2	0	48.51	53.34
4	0	0	-2	0	22.57	14.47
5	-1	1	1	1	80.37	74.70
6	-1	1	-1	-1	12.63	8.12
7	1	-1	-1	-1	25.56	417.46
8	1	-1	-1	1	71.16	61.62
9	-1	-1	-1	-1	13.25	8.75
10	-1	-1	-1	1	62.33	52.21
11	0	2	0	0	23.15	25.01
12	-2	0	0	0	35.52	36.47
13	1	-1	1	-1	27.65	30.42
14	0	0	0	0	58.59	55.59
15	0	0	0	0	60.56	55.59
16	1	1	-1	1	62.55	46.33
17	-1	1	-1	1	61.58	44.62
18	0	0	0	0	59.20	55.59
19	1	1	1	-1	25.56	27.20
20	1	1	1	1	81.25	74.85
21	1	1	-1	-1	19.84	9.80
22	0	0	0	0	58.56	55.59
23	2	0	0	0	43.01	45.40
24	0	-2	0	0	35.12	36.60
25	1	-1	1	1	91.10	85.78
26	-1	-1	1	-1	20.83	23.22
27	-1	-1	1	1	82.69	78.56
28	0	0	0	0	60.78	55.59
29	-1	1	1	-1	27.53	26.89
30	0	0	0	0	61.03	55.59
31	0	0	0	-2	17.98	14.21

^aExperimental, ^bPredicted

Table 3. Analysis of variance (ANOVA) for VOC oxidation conversion

Source of variations	Sum of squares	Degree of freedom	Mean square	Ration of mean squares (F value)
Regression	17580.1	14	1255.72	32.4
Residuals	621.2	16	38.82	
Total	18201.3	30		

$$R^2=0.949; R^2(\text{adj})=0.951$$

used to correlate the dependent and independent variables:

$$Y=b_0+b_1x_1+b_2x_2+b_3x_3+b_4x_4+b_{12}x_1x_2+b_{13}x_1x_3+b_{14}x_1x_4+b_{23}x_2x_3+b_{24}x_2x_4+b_{34}x_3x_4+b_{11}x_1^2+b_{22}x_2^2+b_{33}x_3^2+b_{44}x_4^2 \quad (7)$$

where Y is a response variable of oxidation conversion. The b_i are regression coefficients for linear effects; b_{ii} the regression coefficients for squared effects; b_{ik} the regression coefficients for interaction effects and x_i are coded experimental levels of the variables.

A central composite experimental design, with eight axial points ($\alpha=2$) and seven replications at the center point leading to a total number of 31 experiments was used for response surface modeling. The experimental results and predicted values for ethyl acetate removal efficiencies are presented in Table 2.

Based on these results, an empirical relationship between the response and independent variables was obtained and expressed by the following second-order polynomial equation:

$$Y=55.9474+2.2339x_1-2.2987x_2+10.7416x_3+22.9729x_4-1.7505x_1x_2-0.3701x_1x_3-0.0014x_1x_4+1.0890x_2x_3-1.9065x_2x_4+2.7991x_3x_4-3.7527x_1^2-6.2857x_2^2-5.0214x_3^2+1.0531x_4^2 \quad (8)$$

Table 3 shows the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). ANOVA is required to test the significance and adequacy of the model. These results showed that the regression model had a high value of coefficient of determination ($R^2=0.949$). The R^2 -value provides a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. This implies that 94.9% of the variations for VOC oxidation conversion are explained by the independent variables and that the model does not explain only about 5% of variation.

The Pareto analysis gives more significant information to interpret the results. In fact, this analysis calculates the percentage effect of each factor on the response, according to the following relation [34,35]:

$$P_i=\left(\frac{b_i^2}{\sum b_i^2}\right)\times 100 \quad (i\neq 0) \quad (9)$$

Fig. 1 shows the Pareto graphic analysis. The results of this figure suggest that among the variables, b_3 (70.48%) (reaction temperature), b_4 (15.40%) (calcination temperature) and squared effect of Fe (b_{22} , 7.98%) produce the largest effect on VOC oxidation conversion. Fig. 2 shows a comparison between calculated and experimental values of the response variable of VOC oxidation conversion (Table 2) by using resulted second-order polynomial equation (Eq. (7)). This plot has correlation coefficient of 0.949. Results confirm that the experimental values are in good agreement with the predicted

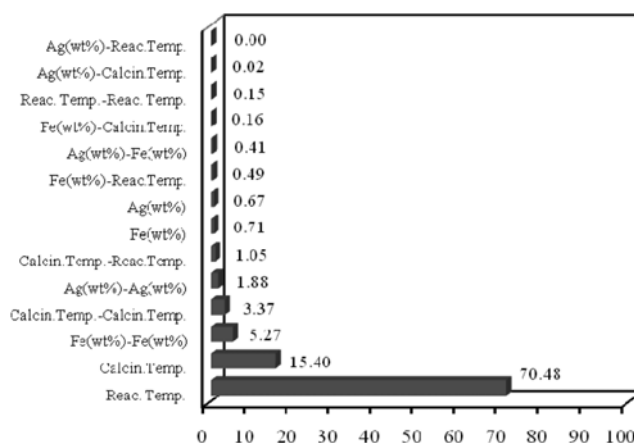


Fig. 1. Pareto graphic analysis.

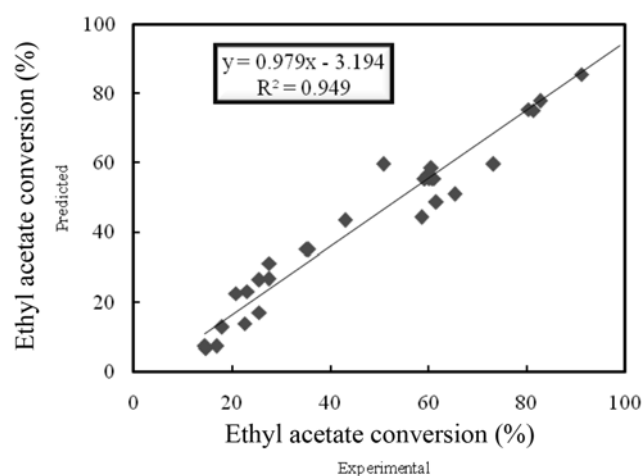


Fig. 2. Comparison of the experimental results of ethyl acetate Conversion with those calculated via central composite design resulted equation.

values.

2. Response Surface and Contour Plots for Catalytic Oxidation of Ethyl Acetate

The response surface and contour plots of the model-predicted responses, while two variables kept at constant and the others varying within the experimental ranges, were obtained by the Minitab software and utilized to assess the interactive relationships between the process variables and treatment outputs for oxidation of ethyl acetate. Response surface plots provide a method to predict the oxidation of ethyl acetate conversion for different values of the tested variables and the contours of the plots and help in identification of the type of interactions between these variables [35]. Each contour curve represents an infinite number of combinations of two tested variables with the other two maintained at their respective zero level. A circular contour of response surfaces indicates that the interaction between the corresponding variables is negligible. In contrast, an elliptical or saddle nature of the contour plots indicates that the interaction between the corresponding variables is significant [28].

2-1. Effect of Ag Loading and Calcination Temperature on Conversion of Ethyl Acetate

Fig. 3 shows the response surface and contour plots for conver-

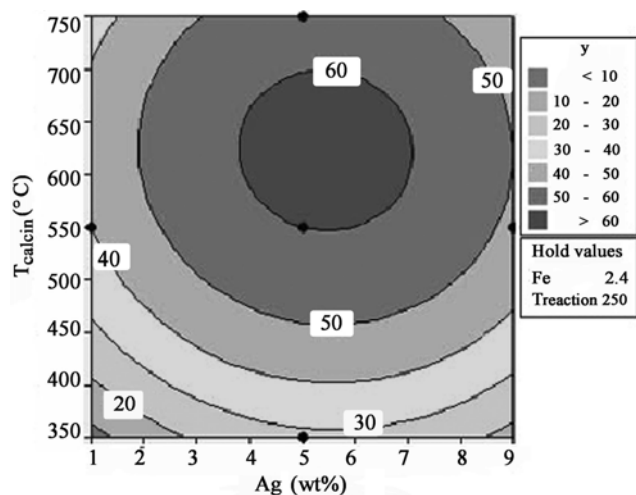


Fig. 3. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of Ag loading (wt%) and calcinations temperature (°C).

sion of ethyl acetate conversion as a function of Ag loading (wt%) and calcinations temperature for Fe loading 2.4 wt% and reaction temperature 250 °C. As can be seen from Fig. 3, the highest conversion (>60%) occurred when Ag loading (wt%) and calcinations temperature were kept at about 4-7 wt% and 550-650 °C, respectively. When Ag loading is lower, the active sites are not enough to catalyze the reaction and when Ag loading is higher agglomeration of metals occurs and it causes blockage of the pores and active sites of zeolite and decreases the catalytic activity of catalyst.

The detrimental effect on the catalytic activity after calcination at 650 °C was probably due to both the reduced porosity, leading to higher mass transfer limitations and the lower dispersion of the active phase due to the lower specific surface area and growth in metal particle size. The influence of the metal particle size on the catalytic activity for complete oxidation of hydrocarbons over supported metal catalysts is still a controversial subject. Depending on the nature and dimensions of the hydrocarbons molecule to be abated,

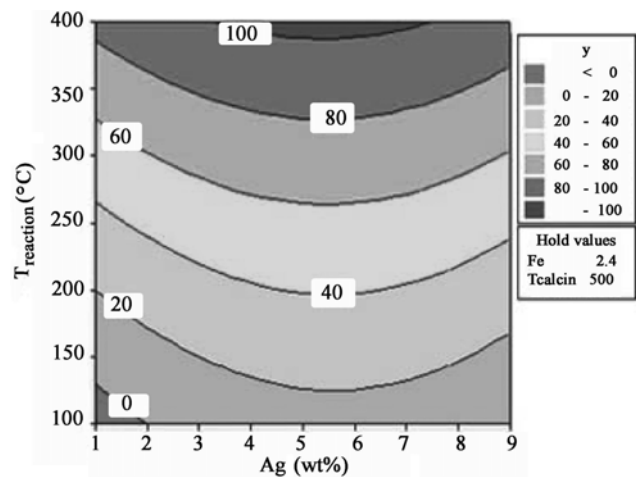


Fig. 4. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of Ag loading (wt%) and reaction temperature (°C).

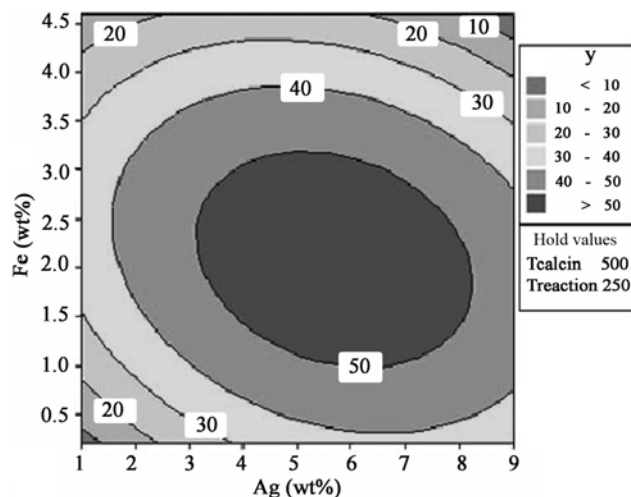


Fig. 5. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of Ag and Fe loading rate (wt%).

the metals active phase and the nature of the support may all play a role in the structure sensitivity of hydrocarbon catalytic combustion. From the results reported here, although high temperature heat calcination caused a rise in the metal particle size there was a reduction in the measured activity. Thus, the reduction in activity would appear to be related to the reduction in the metal dispersion.

2-2. Effect of Ag Loading and Reaction Temperature on Conversion of Ethyl Acetate

Percent conversions for oxidation of ethyl acetate with Fe loading 2.4 wt% and calcination temperature 500 °C obtained as a function of Ag loading and reaction temperature are depicted in Fig. 4. As it is clear from this figure, conversion reached the highest value (100%) when reaction temperature and Ag loading were about 400 °C and 3-7 wt%, respectively.

2-3. Effect of Ag and Fe Loading Rate on Conversion of Ethyl Acetate

Fig. 5 illustrates the effect of silver and iron loading rate on removal conversion of ethyl acetate in the calcination temperature 500 °C and reaction temperature 250 °C. As can be understood from Fig. 5, optimum values of these metals are required for loading on HZSM-5: first, the active sites are provided for the reaction; second, the active sites don't overlap. Results showed that when iron and silver is less on HZSM-5, amount of ethyl acetate conversion efficiency is low, because the numbers of active sites on HZSM-5 are less.

Conversion efficiency gradually increased with increasing metals on HZSM-5, but the large increase in iron and silver content led to low conversion efficiency. So metals loaded on zeolite HZSM-5 play an important role in the oxidation reactions. This is because the activation energy with increasing temperature for oxidation processes provided will be faster and the higher temperatures (>350 °C) provide better conditions.

2-4. Effect of Fe Loading and Calcination Temperature on Conversion of Ethyl Acetate

Fig. 6 presents the response surface and contour plots as an estimate of conversion efficiency as a function of the two process vari-

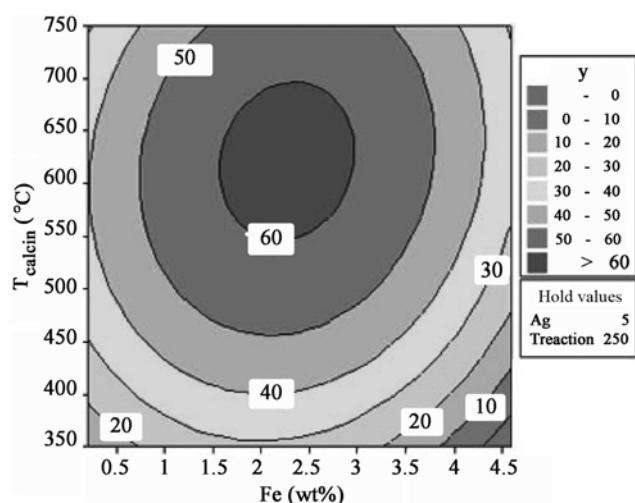


Fig. 6. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of Fe loading (wt%) and calcination temperature (°C).

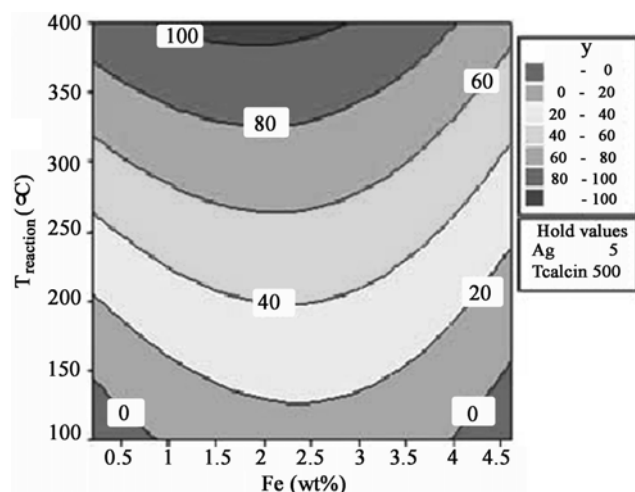


Fig. 7. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of Fe loading (wt%) and reaction temperature (°C).

ables Fe loading and calcinations temperature (Ag loading=5 wt%; Reaction temperature 250 °C). As is obvious from Fig. 6, conversion efficiency increased with increase in Fe loading and reached 60% in 2 wt% of Fe loading.

2-5. Effect of Fe Loading and Reaction Temperature on Conversion of Ethyl Acetate

Fig. 7 displays the 2D plot for conversion efficiencies as a function of Fe loading and reaction temperature (at a fixed Ag loading of 5 wt% and calcination temperature of 500 °C). As it is clear from the response surface and contour plots, conversion efficiency reached

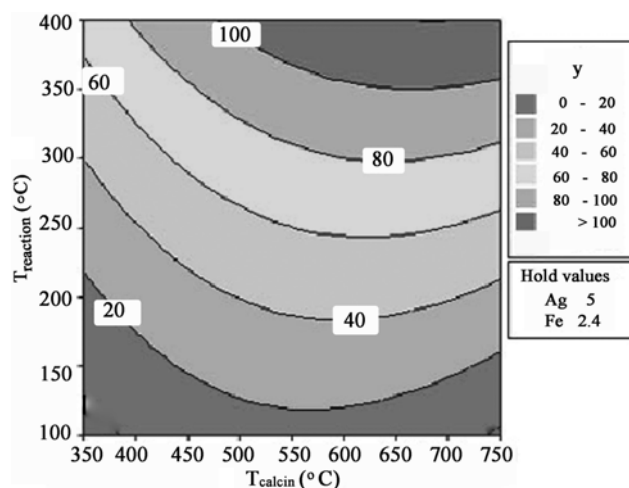


Fig. 8. The response surface plot and contour plot of the conversion of ethyl acetate (%) as the function of reaction and calcination temperatures (°C).

high values (>95%) in a reaction temperature of 350 °C and Fe loading of 2 wt%. This is because the activation energy of catalyst with increasing of temperature for the oxidation processes is provided faster.

2-6. Effect of Reaction and Calcinations Temperatures on Conversion of Ethyl Acetate

Fig. 8 shows the response surface and contour plots for conversion as a function of reaction and calcinations temperatures for Ag and Fe loading 5, 2.4 wt%, respectively. As can be seen, the highest conversion occurred when reaction temperature was kept at about 350 °C under all calcinations temperature conditions.

2-7. Determination of Optimal Conditions for the Conversion of Ethyl Acetate

The desired goal in terms of conversion was defined as to “maximize” to achieve the highest treatment performance. The optimum values of the process variables for the maximum conversion are shown in Table 4. After verifying by a further experimental test with the predicted values, the result indicated that the maximal conversion was obtained when the values of each parameter were set as the optimum values, and the proposed model equation using RSM has shown good agreement with the experimental data, with a correlation coefficient (R^2) of 0.949. It implies that the strategy to optimize the oxidation conditions and to obtain the maximal conversion by RSM for the oxidation of the ethyl acetate as a VOC whit bi-metal Fe-Ag-ZSM-5 catalyst in this study is successful.

CONCLUSIONS

An empirical relationship between the response and independent variables was attained and expressed by the second-order polynomial equation based on results. Analysis of variance showed a high

Table 4. Optimum values of the process parameters for maximum conversion efficiency (desirability factor=1)

Observed conversion conversion (%)	Predicted conversion conversion (%)	Calcination temperature (°C)	Reaction temperature (°C)	Ag loading (wt%)	Fe loading (wt%)
96	97.2	580	350	5.17	2

coefficient of determination value ($R^2=0.949$), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The Pareto graphic analysis suggested that among the variables, reaction temperature, calcinations temperature and squared effect of Fe-Fe produce the largest effect on VOC conversion. Effect of experimental parameters on the conversion of ethyl acetate was established by the response surface and contour plots of the model-predicted responses. The optimum values of the Fe loading, Ag loading, calcination temperature and reaction temperature concentration were found to be 2 wt%, 5.17 wt%, 580 °C and 350 °C, respectively. This study clearly showed that response surface methodology was one of the suitable methods to optimize the operating conditions and maximize the VOC removal.

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