

BTX Hydrogenation in liquid phase using nanoparticles of Cobalt/MWCNTs and data analysis using RSM method

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Abstract

BTX compounds (Benzene, toluene and xylenes) are the main pollutants in air and fuels. Recent environmental legislations are limited the amount of these materials specially the amount of benzene in gasoline due to its carcinogen effects on health. In this research, the BTX hydrogenation was carried out using nanoparticles of Co supported on MWCNTs (multiwall carbon nanotubes) and AC (activated carbon) in liquid phase according to experimental design techniques and results were analyzed by response surface methodology (RSM). The benzene, toluene and xylenes are hydrogenated to the corresponding saturated compounds at 64.45, 34.10 and 17.41 % yields respectively under 35 bar pressure at 200 °C. Also it is found that the Co/MWCNTs can be considered as candidate catalyst for benzene reducing in gasoline fuel. The catalysts were synthesized through wet impregnation method and characterized using XRD, TGA, TPR and TEM techniques.

Keywords: BTX, MWCNT, catalyst, XRD, TGA, TRP, TEM

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1. Introduction

Aromatic BTX compounds (benzene, toluene and xylene) in gasoline fuel are known as most dangerous and main pollutants compounds in air due to their chronic toxicities.¹ According to the MSAT (Mobile source air toxicity) legislations, several numbers of countries reduce the amount of benzene in their gasoline.²⁻⁴ Gas phase catalytic hydrogenation of benzene, toluene and xylenes has been investigated over different supported by Pd,^{5, 6} Ni,^{7, 8} Rh,⁹ and Pt.^{10, 11}

In recent years, a new investigation in application of mesoporous materials such as carbon nanotubes and MCM-41 (Mobil Composition of Matter) as supports for various metals and other catalytic active species is opened.^{12, 13} Carbon nanotubes (CNTs) due to small dimensions, good mechanical strength, high external surface area and their remarkable physical properties have been used as an modern effective support for Ru, Pt, Rh and Pd metals in heterogeneous, homogeneous and electrocatalysts.¹⁴⁻¹⁷

In this contribution, the Co supported on MWCNTs and AC is prepared through wet impregnation method

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from cobalt nitrate hexahydrate and their catalytic activities were investigated in BTX hydrogenation. The experiments were designed according to the experimental design techniques and results were analyzed by response surface methodology (RSM).

2. Materials and methods

Synthesis

All used chemical reagents including Co (NO₃)₂.6H₂O, benzene, toluene, xylene (mixture of ortho, meta and para xylene) and n-heptane have analytical grade. Multiwall carbon nanotubes with purity more than 95% were purchased from research institute of petroleum industry (RIPI) and purified according to our previous work.¹⁸ Activated carbon (AC) with surface area of 1200 m²/g was used from Aldrich Company. *Instruments*

Mettler Toledo TGA SDTA 851e, ASAP-2000 system from Micrometrics quantasorb, Philips ZEISS EM900 at an accelerating voltage of 100 kV, Philips instrument with graphite monochromatic Cu K α radiation (λ = 1.5418 Å) and Micrometrics 2900 system were used for measurement of TGA, ASAP, TEM, XRD and TPR analysis respectively. The yield of products was determined by SRI 8022C Gas chromatography (GC) instrument with flame ionization detector (FID) and MXT-624 capillary column (6% cyanopropylphenyl-94% dimethylsiloxane; 30 m × 0.53 mm I. D, 3 μ m film thicknesses).

Catalyst preparation and catalyst activation

The nanocatalysts of Cobalt at loading of 45% were prepared by incipient wet impregnation method with aqueous solution of cobalt nitrate hexahydrate as described in our earlier work.¹⁸ The prepared cobalt oxide (CoO and Co₃O₄) supported on MWCNTs or AC was converted to the Co/MWCNTs or Co/AC as active catalyst according to TPR program under H_2 at 400 °C for 1h and then the reactor cooled to room temperature.

BTX hydrogenation

Hydrogenation was performed using 0.1 g of above reduced catalyst in 100 mL stainless steel autoclave reactor. About 3 mL of BTX mixture (1mL of each of benzene, toluene and xylene) and 15 mL of n-heptane was transferred to the reactor under N_2 and then purged three times with N_2 . The experiments were carried out at three levels of pressure, temperature and time (Table 1) according to the conditions detailed in Table 2. The yield of products was determined by GC instrument with flame ionization detector (FID) and MXT-625 capillary column at column temperature of 60 to 160 °C at a rate of 4 °C/min.

Experimental design and mathematical modeling

The central composite design (CCD) and RSM method analysis were applied to investigate the effects of operating variables and optimization of conditions. The three operations and process factors containing pressure / bar (25-35), temperature / °C (160-200) and reaction time / min (30-60) were introduced with the most significant impact which was considered as variables of system and yield of products containing cyclohexane (CH), methylcyclohexane (MCH) and dimethylcyclohexane (DMCH) were determined as process responses.

The experiments were designed consisted of 2^k factorial points augment by 2k axial points and a center point, where k is the number of variables. The three levels are: -1 (minimum), 0 (center) and +1 (maximum). The number of 20 experiments ($2^k + 2k + 6$) where k is the number of factors organized in a factorial design (including 8 factorial points, 6 axial points and 1 center point) and remaining of 5 involving the replication of the central point to get a good estimate of the experimental error.¹⁹ Analysis of variance (ANOVA) was used for graphical analyses of data to obtain the interaction between process variables and responses. The response surface methodology technique was applied to understand the interaction of various variables (pressure, temperature and time) and then used to find the optimum conditions of main variables that affect the response and also give equation to predict the yield of products in other condition with high confidence of accuracy.

3. Results and discussion

X-ray and TEM image of cobalt oxide/MWCNTs

The XRD spectrum of synthesized cobalt oxide on MWCNTs was taken in the range of 10-90° (Figure 1). The characteristic peak at $2\theta = 31.08$ was assigned to MWCNTs and other peaks at 21.10, 36.8, 41, 51, 70

and 78° were assigned to mixture of cobalt oxides (CoO and Co₃O₄) based on comparison with JCPDS NO: 9-0418 standard spectrum.²⁰ The average particle size of Co₃O₄ is 20 nm was calculated by Deby-Scherrer equation that is in agreement with TEM analysis (Figure 2).



Figure 1. XRD spectrum of cobalt oxides on MWCNTs.



Figure 2. TEM of cobalt oxides on MWCNTs



Figure 3. TGA and DTG of cobalt oxide on MWCNTs

Table 1. Accelerated surface area and	porosimetery	(ASAP) of s	vnthesized catalyst
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Catalyst	BET(m ² g ⁻¹)	Pore Volume (cm ³ g ⁻	Microspore Area (m ² g ⁻¹)	A.P.D	A.A.P.D	D.A.P.D
		1)		(A°)	(A°)	(A°)
Co ₃ O ₄ /MWCNTs	184.20	0.57	11.36	123.65	118.2	108.35
Co ₃ O ₄ /AC	511.4	0.34	279.10	39.15	73.4	69.60
MWCNTs	270.0	-	-	-	-	-

A.P.D = Average Pore Diameter (4V/A by BET)

AAPD = Adsorption Average Pore Diameter (4V/A)

DAPD = Desorption Average Pore Diameter (4V/A)

TGA Analysis of Co₃O₄/MWCNTs

The synthesized cobalt oxide supported on MWCNTs was examined under atmosphere of N₂ from 30-800 °C at a rate of 10 °C/min and weight changes are recorded as TGA and DTG in Figure 3. The first major weight loss was observed at about 100 °C which mainly corresponded to the loss of physisorbed H₂O in the sample and after that until 600 °C the weight change is not observed. The second and the main weight loss were occurred at 600-800 °C which attributed to the loss of amorphous carbon in nanotubes network. As it is shown in this Figure more than 80 % of MWCNTs structure at 800 °C is remained unchanged. It indicates that the catalyst is resistant to thermal decomposition until 600 °C and can be applied as catalyst in both liquid and gas phase reactions from ambient temperature to 600 °C.

BET analysis of catalysts

The specific surface areas of the synthesized compounds calculated by BET method are 270.0, 184.2 and 511.4 m²/g for MWCNTs, $Co_3O_4/MWCNTs$ and Co_3O_4/AC respectively. The results of accelerated surface area and porosimetry (ASAP) are listed in Table 1. The results show that the micropore area of the $Co_3O_4/MWCNTs$ and Co_3O_4/AC are 11.36 and 279.10 m²/g respectively that indicates the 6.16 and 54.57 % of total area in MWCNTs and AC support is in micropore state respectively.

The H₂-TPR profile of cobalt oxide on MWCNTs was performed in a quarts reactor. The sample was heated from 25 to 830 °C at a rate of 10 °C/ min and swept with 95% Ar-5% H₂ (by volume). The hydrogen concentration was detected by TCD detector. The TPR analysis revealed that the cobalt oxides were reduced to Co metal at 450°C.

BTX Hydrogenation

Benzene, toluene and xylene due to the presence of aromatic ring in their structures are resistant to hydrogenation. The hydrogenation related to the kind of applied catalyst and reaction conditions can be proceed through partial or complete reduction. Overall BTX hydrogenation is illustrated in Scheme 1.



 $\label{eq:R1} R_1{=}H\,, CH_3 \quad R_2{=}\,H\,, CH_3$ Scheme 1. Public schematic of BTX hydrogenation

Table 2. Experimental range and levels of the independent variables								
	Ranges and levels							
Variables	-α (-1)	0	+α (+1)					
A: Pressure / bar	25	30	35					
B: Temperature / °C	160	180	200					
C: time / min	30	45	60					

Table 2. Experimental range and levels of the independent variables

In this work, the reactions were carried out in a batch reactor containing three phases including liquid phase of BTX, solid phase of catalyst and gaseous phase of hydrogen. The reactions were carried out in n-heptane as inert solvent using Co/MWCNTs and Co/AC at loading of 45 % and by products from partial hydrogenation or isomerization are not detected.

Model fitting and statistical analysis

The variables and their levels in BTX hydrogenation are shown in Table 2. The experimental data for BTX hydrogenation in a batch reactor system with Co/MWCNTs and Co/AC are given in Table 3. The relationship between effective parameters containing pressure, reaction time, temperature and yield of products was analyzed by RSM. It is observed that the predicted values from model fitting technique are sufficiently correlated to the observed values and slightly deviated from experimental data. Fitting of data to various models (linear, two factorial, quadratic and cubic) and their subsequent analysis of variance (ANOVA) shows that the BTX hydrogenation was most suitably described by quadratic polynomial model for Co/MWCNTS and linear for Co/AC.

Multiple regression coefficients of a second-order polynomial model of BTX hydrogenation are summarized in Table 4. The significance of each coefficient was determined by F-value and P-value.²¹The corresponding P-values suggest that the significant model terms for BTX hydrogenation are A, B, C, AB, BC, AC, A², B², C² with Co/MWCNTs and A, B,C with Co/AC.

Run Variables				Co/MW	CNTs					Co/AC		
				%C	Н	%MC	Н	% DN	1CH	%CH	%MCH	% DMCH
	\mathbf{P}^{a}	T^{b}	t ^c	Actual	predicte	Actual	predicte	Actual	Predicte	Actual	Actual	
					d		d		d			Actual
1	30	180	45	50.18	49.96	25.68	25.07	12.40	12.25	14.25	7.11	3.80
2	21.5	180	45	33.38	32.11	21.61	19.64	4.50	3.85	10.10	5.45	1.10
3	30	180	45	50.32	49.96	25.32	25.07	13.10	12.25	15.75	7.95	5.25
4	30	180	45	50.20	49.96	25.57	25.07	12.25	12.25	14.05	8.25	4.95
5	38.5	180	45	57.65	58.95	29.33	29.24	14.23	13.61	20.25	10.20	4.65
6	30	180	45	51.10	49.96	25.75	25.07	11.90	12.25	15.70	8.05	3.85
7	25	160	60	39.92	39.90	27.55	29.04	7.84	8.76	12.15	7.10	3.14
8	30	180	19.5	40.33	40.79	19.80	21.32	8.15	7.65	13.20	5.80	3.22
9	30	180	45	50.72	49.96	23.42	25.07	13.10	12.25	18.35	9.05	5.80
10	25	200	30	34.28	34.30	14.35	14.64	2.05	2.91	10.50	7.15	0.00
11	25	160	30	24.58	24.26	10.71	10.54	1.60	1.55	8.20	4.75	0.00
12	30	146	45	20.60	22.28	6.75	6.85	0.00	0.24	4.05	2.10	0.00
13	30	214	45	53.37	53.72	27.16	24.99	13.40	12.70	23.90	10.50	6.43
14	35	160	30	31.32	32.83	14.07	12.60	2.05	2.85	9.35	4.34	0.00
15	35	160	60	38.84	37.80	17.31	18.51	3.10	3.16	10.25	6.23	0.70
16	25	200	60	40.28	41.75	23.56	26.53	7.11	7.23	15.75	11.21	4.05
17	35	180	30	56.10	59.96	31.35	35.07	15.75	16.25	19.32	11.80	6.15
18	35	200	60	64.45	64.75	34.10	35.76	16.45	17.41	21.30	13.57	6.80
19	30	180	70	51.77	51.35	40.04	36.46	12.35	11.58	22.04	11.05	4.35
20	30	180	45	51.10	49.96	28.17	25.07	13.10	12.25	18.15	8.80	4.05

Table 3. Experimental conditions and results of central composite design

a: Pressure (bar) , b: Temperature (°C), C: Reaction time (min)

A:B	C.E	S.E	S.S	D.F	M.S	F-value	P-value	
quadr atic	51:15	0.26:0.63	2378:368	9:3	264:123	76.1:15.4	<0.0001: <0.0001	Sig
A	7.5:2.2	0.2:0.80	642:64	1:1	642: 64	206.1:8.0	< 0.0001: 0.0121	Sig
В	9.2:4.4	0.2:0.80	962:244	1:1	962:244	282.7:30.7	<0.0001: <0.0001	Sig
С	3.3:1.9	0.2:0.80	135:20.3	1:1	135:20	31.9:6.1	<0.0001: 0.0258	Sig
AB	6.4:-	0.27:-	237:-	1:1	237: -	66.9:-	<0.0001:-	Sig
BC	-2.4-	0.27:-	33:-	1:-	33: -	7.1:-	<0.0001:-	Sig
AC	-2.0:-	0.27:-	24:-	1:-	24: -	12.1:-	<0.0001:-	Sig
A ²	-1.8:-	0.17: -	47:-	1:-	47:-	10.3:-	<0.0001:-	Sig
B ²	-4.7: -	0.17: -	330:-	1:-	330: -	75.3:-	<0.0001: -	Sig
C ²	-1.6: -	0.17: -	36:-	1:-	36:-	8.0:-	<0.0001: -	Sig
L.F	-	-	3.5:103.7	5:10	0.7:10.4	3.75:2.86	0.0867:0.1229	Not Sig

Table 4. Estimated regression coefficients resulted from ANOVA analysis and central composite design

A: B, Co/MWCNT: Co /AC C.E: Coefficient estimate S.E: Standard error S.S: Sum of squares D.F: Degree of freedom M.S: Mean Square L.F: Lack of Fit Sig: Significant

The following regressions of Eq. (1) and Eq. (2) are the empirical models in terms of coded factors for benzene, toluene and xylene in BTX hydrogenation by Co/MWCNTs and Co/AC respectively.

With Co/MWCNTs:

With Co/AC:

%CH =10.11+0.027 A* + 4.94 B* +1.99 C* +2.82 A*B* -1.84 A*C* -0.64 B*C* **Eq. 2** In Which:

$$A^* = \frac{2(A - A_H)}{A_H - A_L} + 1 \qquad B^* = \frac{2(B - B_H)}{B_H - B_L} + 1 \qquad C^* = \frac{2(C - C_H)}{C_H - C_L} + 1$$

H and L detail high and low amounts of each of variables in table 1.From Table 1: A_H and A_L is 35 and 25, B_H and B_L is 200 and 160 and C_H and C_L is 60 and 30 respectively. It is clear from Eq. (1) that the significant reaction parameters for Co/MWCNTs (most to least significant) are: Temperature (benzene, toluene, xylene: 9.20, 5.34, and 5.30) > Pressure (benzene, toluene, xylene: 7.51, 2.82, and 3.81) > Reaction time (benzene, toluene, xylene: 3.31, 4.45, and 1.57).

Table 5. Analysis of variance (ANOVA) for fitting of CH efficiency from central composite design after elimination of	
insignificant model terms	

Model	Significant model terms	SD	R ²	Adj.R ²	CV%	Adq. precisior	Press	F- Value	P- Value
%CH, Quadratic model for Co/MWCNT	A,B,C, AB,BC,AC, A ² , B ² ,C ²	0.7	0.99	0.99	1.51	92.03	35.2	599	<0.0001
%CH, Quadratic model for Co/AC	A,B,C	2.8	0.74	0.70	19.2	13.76	215	15.8	<0.0001

The ANOVA results of modified quadratic model for benzene hydrogenation (as example) in BTX mixture in Table 5 show that the model could adequately be used to describe benzene at the range of operating conditions. The results indicate that the quadratic model was significant at the 5% confidence level since P-values (0.0001) were less than 0.05. The coefficient of determination (R^2) as a measure of the goodness of fitted model was very significant at the level of 99%. Adequate precision (as signal to noise ratio) for benzene hydrogenation is 92.03 that is an adequate signal. A very high degree of precision and good deal of reliability of the experimental values was indicated by a low value of coefficient of variation (% CV = 1.51 and 19.20 for Co/MWCNTs and Co/AC respectively).

The major diagnostic plots (Figure 4a-c) for benzene hydrogenation as example in BTX mixture are used to determine the residual analysis of response surface design, ensuring the statistical assumptions is fitted with analysis of data. Figure 4a displays the normal probability of the residuals to verify whether the standard deviation between the actual and predicted response values follows a normal distribution. The plots of residual versus predicted responses are shown in Figure 4b. All points of experimental runs were scattered randomly within the constant range of residuals across the graph within the horizontal lines at the point of ± 3.0 . This reveals that the models proposed are adequate and that the constant variance assumption was confirmed. The responses from the experimental results also were fitted well within an acceptable variance range when compared with the predicted values from the respective empirical models (Figure 4c).



Figure 4a-c. (a) Normal probability plot of residual (b) plot of residual versus predicted response (c) predicted vs. actual values plot for CH production



Figure 5. The response surface 3D and contour plots of CH production yield (%) as a function of (a) Temperature (°C) and reaction time (min), (b) Pressure (bar) and reaction time (min) and (c) Temperature (°C) and pressure (bar)

Effect of temperature, pressure and reaction time on BTX hydrogenation

The effects of three variables on benzene hydrogenation as example in BTX mixture are shown in Figure 5a-c in counter plot and 3D diagram. The effect of P and T on the reaction is shown in Figure 5a. The coefficient of both factors on reaction is 6.37 for Co/MWCNTs. Each of P and T factors has the most effect on reaction individually and combination of them also plays important role in reaction. Since the reaction was carried out in the liquid phase, increasing of pressure lead to enhance surface contact of reactants and lead to increasing yield of reaction. Also increasing of temperature prepare activation energy of reaction and lead to increasing of yield. Influence of pressure and reaction time on reaction is shown in Figure 5b.

The pressure coefficient for benzene hydrogenation in BTX mixture using Co/MWCNTs catalyst is 7.51 that indicate the effect of pressure is considerable. Figure 5c shows the CH yield as a function of temperature and reaction time using Co/MWCNTs catalyst. As it is obvious from this Figure, the yield is increased with simultaneous increasing in temperature and reaction time. High coefficient of temperature (B=9.20) indicates that the temperature plays major role in this reaction. Similar results are obtained with Co/AC as detailed in Eq. (2). Also the effects of each variable and overall perturbation are shown in Figure 6a-c and 7 respectively. As shown in Figure 7, the highest slop is observed for temperature that have high coefficient in Eq. (1).

Effect of support

The results in Table 2 show that the cobalt supported on MWCNTs has higher activity than AC support. Since both of these supports are allotropes of carbon, the observed differences can be related to the difference in surface morphology of two supports. As the results indicate in Table 3, the micropore area ratio in MWCNTs is only 6.16 % while in AC support it is about 54.57%. The MWCNTs due to mesopore structure carried out better mass transfer (especially adsorption and desorption in surface of catalyst) which accelerates the hydrogenation reaction in comparison with AC support under similar conditions. Also from the results in table 2, it is understand that a relatively selectivity in BTX hydrogenation is observed for benzene hydrogenation rather than toluene and xylene due to sterric effects. This means that the catalyst is suitable candidate for benzene reduction in gasoline with least decrease in octane number of gasoline because the main portion of aromatics (total aromatics allowed in Euro4 standard IS 35%) in gasoline is related to toluene and xylenes.



Figure 6a-c. Effect of each variables (a) pressure (b) temperature and (c) time on the reaction



Figure 7. Overall perturbations of variables on reaction

Optimization process and model verification

In numerical optimization, the desired goal for each factor and response were chosen. The objective functions are the maximize yields of CH, MCH and DMCH using Co/MWCNTs catalyst in operating ranges of temperature, pressure and time. Several acceptable conditions are listed in Table 6 that we expect to obtain high yield for CH as example in BTX hydrogenation. As illustrated in Table 6 the optimum conditions were obtained in tray 1 under 34.14 bar pressure, 198.01°C and 41.04 min which predicted CH yield is 64.6563 with high desirability of 1.00 (Desirability is an objective function that ranges from zero outside of the limits to one at the goal). Also at high level of variables defined in Table 1 (T=214 °C, P=38.5 bar and time= 70.5 min) according to equation 1 resulted from RSM technique, the highest possible yield for CH, MCH and DMCH are 68.03, 29.93 and 15.22 % respectively.

Tray	P /bar	T/°C	time/min	% CH	Desirability
1	34.14	198.01	41.04	64.6563	1.000
2	34.67	198.87	50.37	65.6049	1.000
3	35.00	200.00	60.00	64.5912	1.000
4	34.85	199.83	30.99	66.0083	1.000
5	34.98	197.97	58.20	64.5725	1.000
6	34.86	196.30	54.37	64.6505	1.000
7	34.73	199.09	55.75	64.9373	1.000
8	34.84	197.71	37.67	65.8411	1.000
9	34.62	196.75	45.14	65.2211	1.000
10	34.82	199.41	46.74	66.3805	1.000
11	34.63	197.62	51.84	65.0181	1.000
12	34.58	196.76	51.03	64.7611	1.000
13	34.24	199.83	51.53	64.8515	1.000
15	34.25	198.74	38.67	65.0046	1.000
15	34.90	199.13	57.98	64.7514	1.000
16	34.68	197.56	42.15	65.6301	1.000
17	34.97	198.89	40.41	66.6936	1.000
18	34.57	198.60	56.04	64.4884	1.000
19	34.32	199.25	51.45	64.8958	1.000
20	34.99	196.02	46.70	65.5627	1.000
21	34.26	198.44	43.96	65.063	1.000
22	34.43	197.73	39.70	65.1072	1.000
23	34.76	198.86	39.67	66.2251	1.000
24	34.91	199.09	57.26	64.9201	1.000
25	35.00	193.13	51.01	64.1184	0.992
26	34.67	195.20	30.00	63.2974	0.974

Table 6. Numerical optimization conditions for benzene hydrogenation using Co/MWCNTs

4. Conclusion

It can be concluded that the Co/MWCNTs has higher activity than Co/AC and also it can be considered as effective catalyst in BTX hydrogenation especially as candidate catalyst for benzene reduction in gasoline. This revealed that the MWCNTs due to mesoporous structure carried out better mass transfer which led to increasing in the yield of reaction. Clean reaction, single product, lack of isomerization and simplicity in isolation of products and liquid phase reaction are the advantages of this method for BTX hydrogenation.

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