

Acid activated bentonite as a green catalyst for synthesis of coumarin derivatives

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Abstract: In this study, acid modified bentonite was applied as a catalyst for synthesis of coumarins via the Pechmann reaction. Various factors such as reaction temperature, amount of catalyst, and reaction time affecting the reaction yields were investigated using experimental design methodology. These factors were modeled by central composite design (CCD) and then the response surface plots were depicted based on the defined model. The optimum conditions were identified by Nelder-Mead non-linear optimization. Under the optimum conditions, i.e., 0.05 g for the amount of catalyst, 85 °C for the reaction temperature, and 30 min for reaction time; the experimental reaction yield was 98.0 ± 4.1 , in agreement with the model predicted reaction yield (98.5 ± 2.4). The results showed that the acid modified bentonite acted as a highly efficient, stable and reusable catalyst for coumarin synthesis under solvent-free conditions at 85 °C. In addition of being eco-friendly, low cost, non-toxic, and reusable properties of the catalyst, high yields with easy work-up and purification of products by non-chromatographic methods are other advantages.

Keywords: Modified bentonite; Green catalyst; Coumarin derivatives; Multivariate optimization; Central composite design.

INTRODUCTION

Coumarins and their derivatives which represent an important class of organic heterocyclics, have medical applications and can be found in many natural or synthetic drug molecules. They also possess versatile biological activities [1, 2]. Due to their sufficient fluorescence in the visible light range, large Stokes shift, high quantum yield; they have been extensively investigated [3, 4].

Plants are the most important natural source of coumarins, but extraction from plant is tedious, time consuming and needing more elaborate setup. Therefore, the synthetic methods, including Pechmann and Knoevenagol condensation [5, 6], Claisen rearrangement [7] and Wittig, Perkin and Reformatsky reactions [8-10] have been developed for synthesis of coumarins. Pechmann condensation has been the most widely applied procedure, since it proceeds from simple starting materials (phenol and β -keto ester) through an acid catalyzed and producing high yields. Generally, concentrated sulfuric acid, trifluoroacetic acid, or phosphorous pentoxide [5, 11 and 12] are used as catalyst for the synthesis of coumarin and their derivatives. Beside these, uses of different other homogeneous catalysts like metal chlorides and sulfonic acid were reported as acid catalysts for the Pechmann condensation reaction [13-17]. However, most of these acid catalysts are required in stoichiometric amounts or in excess for high yield, which due to their corrosiveness, difficulty in separation and creating severe environmental problems regarding disposal of post reaction wastes are unsuitable.

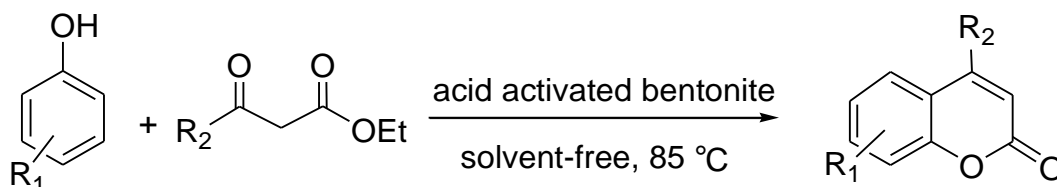
To address the above inherent limitations of homogeneous systems, heterogeneous solid systems are the appropriate as they are easily recoverable, reusable and minimized the wastes. A diverse array of supported catalysts and solid acids, such as resins [18], clays [19], nafion resin/silica composite [20], amberlyst ion-exchange resins [21], silica supported perchloric acid [22], functionalized mesoporous silica (e.g. Zr-TMS, Al-MCM-41) [23,24], nano-crystalline sulfated-zirconia [25], Polyaniline-sulfate salts [26] and Mesoporous zirconium phosphate [27] have been developed and used by several groups to catalyze the Pechmann reaction with different degrees of success. However, these protocols do not always lead to satisfactory results, and they generally require longer reaction times and higher reaction temperatures than the homogeneous catalyst systems. And also these solid acid catalysts have other disadvantages like poor thermal stability, lack of reproducibility, complex separation, low surface area, less water tolerance ability and small pores for large-size reactants for which large amount of catalyst is required to produce high yield [19, 20, 25]

Therefore, it seems that there is still a lot to develop new methods based on recyclable catalysts under more appropriate reaction conditions.

In the last two decades, science and technology have devoted to the introduction and applications of eco-friendly processes that minimize pollution and maximize sustainable development in chemical synthesis [28]. In this respect, solid acids have been introduced several important advantages such as removal, recovery, and reutilization of catalysts, reduced environmental contamination, good thermal and chemical stabilities, and good dispersion of the active catalytic site [29]. Recently, clays as nano structured materials have been widely used in organic transformations as solid acid catalysts [30].

The mineral clays, such as bentonite, montmorillonite, smectite, kaolinite, sepiolite, and zeolite are being considered as catalyst due to their unique chemical and physical properties like mechanical and thermal stability, high surface area and ion exchange capacity. Among these clays, bentonite is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. There are many negative charges on the surface of bentonite due to either the isomorphous substitutions of Al³⁺ for Si⁴⁺ in the tetrahedral sheets or Mg²⁺ for Al³⁺ in the octahedral sheets. Such negative charges are balanced by the presence of exchangeable cations like Na⁺, Ca²⁺, etc. in bentonite lattice structure [31]. Bentonite structural modification has been focused on organobentonite, bentonite modified with a cationic surfactant, polymer, or chitosan, thermal treatment, acid activation and pillaring [32, 33]. The profitability of modified bentonite is now well-recognized because of their ease of modification, non-corrosiveness, ease of workup and separation of products and catalysts, especially from the economical point of view, and their applications in industrial processes.

Regarding the above clarifications and our interest and our experience in the area of heterogeneous catalysis in organic synthesis [34-38], we have developed an acid modified bentonite as a novel green catalyst for the synthesis of coumarins under solvent-free condition (scheme 1).



Scheme 1. Synthesis of 4-substituted coumarins using acid activated bentonite

Experimental

General

Chemicals were purchased from Merck and Fluka chemical companies. IR spectra were recorded on KBr pellets on a PerKin-Elmer IR-783 spectrophotometer. ¹H and ¹³C spectra were determined on a Bruker Avance DPX spectrometer at 250 and 62.90 MHz (CDCl₃ or DMSO solution). Mass spectra were recorded on a GC 17A, MS QP 5050 Shimadzu instrument. Melting points were measured on an electrothermal 9200 apparatus in open capillary tubes. All the reactions were monitored by thin layer chromatography (TLC) on pre-coated sheets of silica gel G/UV-254 using UV light for visualization.

Acid modification of bentonite

A natural Na-bentonite clay (Birjand, South Khorasan, Iran) was used as the starting material. Natural powder clay was treated under mechanical stirring with HCl solution (0.1 M) at 70 °C for 2 h in a 500 mL reactor under reflux conditions. After activation the solids were washed until pH>3, dried at 105 °C, and ground to pass through a 125 μm sieve and then were used. The number of H⁺ site of acid modification of bentonite determined by acid–base titration was 0.1 meq/g

General procedure for preparation of 4-substituted coumarins

To a mixture of phenolic substrate (1 mmol) and β- Keto-esters (1 mmol) acidic modified bentonite (0.500g equal to 0.05 mmol of H⁺) was added and magnetically stirred at 85 °C. The progress of the reaction was followed by TLC. After the completion of the reaction warm ethanol (2×10 mL) was added and the mixture stirred for 5 min and filtered. Ethanol was evaporated under reduced pressure and crude product was recrystallized from hot ethanol. The recovered catalyst was dried and reused

Dihydroxy -4- methyl -2H- chromen-2-one (3b, C₁₀H₈O₄)

Mp 240-242 °C ; IR (KBr): $\nu=3420, 3120, 1620, 1550\text{cm}^{-1}$; $^1\text{H NMR}$ (DMSO- d_6): $\delta = 2.46$ (s, CH_3), 5.81 (s, $\text{C}=\text{CH}$), 6.14(s, ArH), 6.22(s, ArH), 10.27(s, OH), 10.50 (s, OH) ppm; $^{13}\text{C NMR}$ (DMSO- d_6): $\delta = 23.83, 94.95, 99.53, 102.54, 109.27, 155.40, 156.93, 158.36, 160.52, 161.49$ ppm; MS: $m/z(\%) = 192$ (M^+ , 42), 163 (100), 135 (5), 79 (6), 76 (7), 69 (5).

Dihydroxy -4- methyl -2H- chromen-2-one (3c, $\text{C}_{10}\text{H}_8\text{O}_4$)

Mp 280-281°C; IR (KBr): $\nu=3450, 3150, 1670, 1549\text{cm}^{-1}$; $^1\text{H NMR}$ (DMSO- d_6): $\delta = 2.45$ (s, CH_3), 5.80 (s, $\text{C}=\text{CH}$), 6.13(s, ArH), 6.22(s, ArH), 10.29(s, OH), 10.50(s, OH) ppm; $^{13}\text{C NMR}$ (DMSO- d_6): $\delta = 23.85, 94.94, 99.51, 102.53, 109.25, 155.43, 156.92, 158.36, 160.54, 161.48$ ppm.

Hydroxy -4,8-di methyl -2H- chromen-2-one (3e, $\text{C}_{11}\text{H}_{10}\text{O}_3$)

Mp 263-264 °C; IR (KBr): $\nu= 3250, 2910, 1720, 1680, 1620 \text{ cm}^{-1}$; $^1\text{H NMR}$ (DMSO- d_6): $\delta = 2.12$ (s, CH_3), 2.32 (s, CH_3), 6.10 (s, $\text{C}=\text{CH}$), 6.82 (d, $J = 8.8$ Hz, ArH), 7.44 (d, $J = 8.7$ Hz, ArH), 9.5 (s, OH) ppm; $^{13}\text{C NMR}$ (DMSO- d_6): $\delta = 8.24, 18.61, 110.33, 111.11, 112.15, 124.45, 153.20, 155.10, 160.50, 161.48$ ppm; MS: $m/z(\%) = 190$ (M^+ , 28), 161 (100), 133 (12), 105 (14), 91 (19), 75 (31), 62 (30), 50 (33).

Methoxy -4- methyl -2H- chromen-2-one (3f, $\text{C}_{11}\text{H}_{10}\text{O}_3$)

Mp 158-160 °C ; IR (KBr): $\nu= 3070, 3020, 2950, 1610 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 2.40$ (s, CH_3), 3.88 (s, OCH_3), 6.13 (s, $\text{C}=\text{CH}$), 6.75 (s, ArH), 6.83 (d, $J = 8.8$ Hz, ArH), 7.48(d, $J = 8.8$ Hz, ArH) ppm; $^{13}\text{C NMR}$ (CDCl_3): $\delta = 18.64, 55.72, 100.85, 111.97, 112.27, 113.58, 125.49, 152.49, 155.34, 161.25, 162.65$ ppm; MS: $m/z(\%) = 190$ (M^+ , 59), 162 (88), 147 (100), 91 (45), 76 (34), 65 (36), 50 (35).

RESULTS AND DISCUSSION

Preliminary experiments

In continuation of our work on the development of novel synthetic methodologies toward the synthesis of heterocyclic compounds, the catalytic activity of modified bentonite was tested for synthesis of coumarin derivatives. We attempted to find technically simple, high yielding, and solvent-free conditions for the synthesis of these compounds.

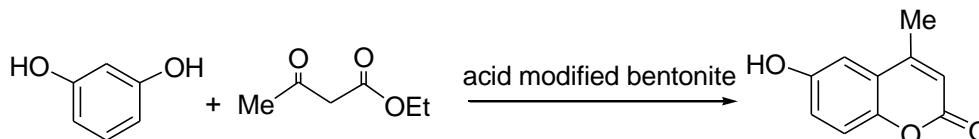
Therefore, we studied acid modified bentonite as a catalyst in the phenol with β -keto ester cyclocondensation. Firstly, the reaction of resorcinol (1 mmol) and ethyl acetoacetate (1 mmol) catalyzed by acid modified bentonite was investigated in different solvents including H_2O , EtOAc, MeOH, EtOH, CH_2Cl_2 as well as under solvent-free conditions, and the results are shown in Table 1.

Table 1 : Effect of solvent on the synthesis of 3a^a.

Entry	Catalyst	Solvent	Time (min)	Yield (%) ^b
1	Bentonite	Solvent free	120	5
2	Acid modified bentonite	Solvent free	30	94
3	Acid modified bentonite	H_2O	30	12
4	Acid modified bentonite	MeOH	30	25
5	Acid modified bentonite	EtOH	30	20
6	Acid modified bentonite	EtOAc	30	20
7	Acid modified bentonite	CH_2Cl_2	30	10

^aReaction conditions: resorcinol (1 mmol) and ethyl acetoacetate (1mmol), in presence of bentonite and acid modified bentonite.

^bIsolated yields.



A great amount of waste in the environment is attributed to the use of organic solvents. Therefore, organic reactions without the use of conventional organic solvents have attracted much attention of synthetic organic chemists. It is worth mentioning that application of solvents didn't lead to better results. Regarding Table 1, entries

3-7, under these conditions, longer reaction times and very low yields obtained. It is observed that the solvent-free conditions gave an excellent yield of product and shorter reaction times than that of in the presence of solvents. Also, cyclocondensation of resorcinol and ethyl acetoacetate was carried out with bare bentonite as catalyst at 85 °C for 2 hour under solvent-free conditions, which resulted in a yield of 5-6% (Table 1, entry 1).

Various factors, e.g. amount of catalyst, temperature, and reaction time, affected the yield of reaction that was performed by using the proposed acid modified bentonite catalyst. In order to find the best condition to achieve the maximum reaction yield, the experimental design was used in the next step.

Table 2: Factors, factor notation, and their levels in BBD

Factor	Notation	Levels				
		$-\alpha^a$	-1	0	+1	$+\alpha$
Amount of catalyst (g)	A	0.010	0.020	0.035	0.050	0.060
Reaction time (min)	B	9.9	15	22.5	30	35.1
Reaction temperature (°C)	C	58	35	65	85	92

$^a\alpha$ value= ± 1.68

Table 3: Design of matrix and responses for CCD.

Run	Block	Amount of catalyst (g)	Reaction time (min)	Reaction temperature (°C)	Yield (%)
1	1	-1	-1	-1	17
2	1	+1	-1	+1	80
3	1	0	0	0	68
4	1	0	0	0	70
5	1	0	0	0	69
6	1	+1	+1	-1	70
7	1	-1	+1	+1	55
8	2	-1	+1	-1	35
9	2	0	0	0	68
10	2	+1	-1	-1	55
11	2	+1	+1	+1	98
12	2	0	0	0	70
13	2	0	0	0	69
14	2	-1	-1	+1	30
15	3	0	0	0	74
16	3	0	+1.68	0	82
17	3	0	0	-1.68	50
18	3	0	0	0	71
19	3	0	-1.68	0	48
20	3	0	0	0	70
21	3	+1.68	0	0	91
22	3	-1.68	0	0	20
23	3	0	0	+1.68	88

Response surface methodology (RSM)

Several classes of RSM such as central composite design (CCD), Box–Behnken design and three-level factorial design have different properties and characteristics that CCD is a more popular rotatable and orthogonal technique applicable for modeling of the main factors and interaction factors with the response. The polynomial regression equation is most prominent relationship for analysis of correlation between factors and response.

Based on preliminary experiments, the best reaction conditions with maximum yield was obtained when the catalyst amount, reaction temperature, and reaction time was in the range of 0.02-0.05 g, 65-85 °C, and 15-30 min, respectively.

Table 2 illustrated the appropriate ranges for these three factors. Due to the small number of factors, there is no need for screening by factorial design, so CCD was used directly. This design is performed using a combination of factorial points ($N_f = 2^f$), axial points ($N_a = 2f$), and a set of center points (N_c), so that 23 experiments containing 8 factorial points, 8 axial points, and 9 replications of the center point were carried out (Table 3). In all of these runs, the reaction was done under solvent-free condition, and the yields of reaction as response were obtained, and the data were analyzed by Design Expert 8. It was found that the best fitted model was quadratic.

The value of regression coefficient was calculated using backward mode of multiple linear regression (MLR) models to exclude non-significant effects from the model to avoid over-fitting. Then, the yield of reaction was related to amount of catalyst, reaction temperature, and reaction time by using the following overall predictive model in terms of coded factors (Eq.1).

$$\text{Yield}(\%) = +69.93 + 20.90A + 9.75B + 10.98C + 2.50AC - 6.81A^2 - 3.45B^2 - 2.04C^2 \quad (1)$$

Table 4: Analysis of variance (ANOVA) for CCD.

Factor	SS ^a	df ^b	MS ^c	F-Value	p-Value
Model	9963.6	9	1107.1	270.0	<0.0001
A	5964.6	1	5964.6	1449.8	<0.0001
B	1298.8	1	1298.8	315.7	<0.0001
C	1645.5	1	1645.5	400.0	<0.0001
AB	12.5	1	12.5	3.0	0.1092
AC	50.0	1	50.0	12.1	0.0051
BC	12.5	1	12.5	3.0	0.1092
A ²	736.0	1	736.0	178.9	<0.0001
B ²	189.0	1	189.0	45.9	<0.0001
C ²	65.8	1	65.8	16.0	0.0021
Residual	45.3	11	4.1		
LOF	32.6	5	6.5	3.1	0.1012
Pure Error	12.7	6	2.1		
Cor Total	10147.0	22			
Model statistics					
R ²	0.9955				
R ² _{adj}	0.9918				
R ² _{pred}	0.9768				

^a Sum of Square

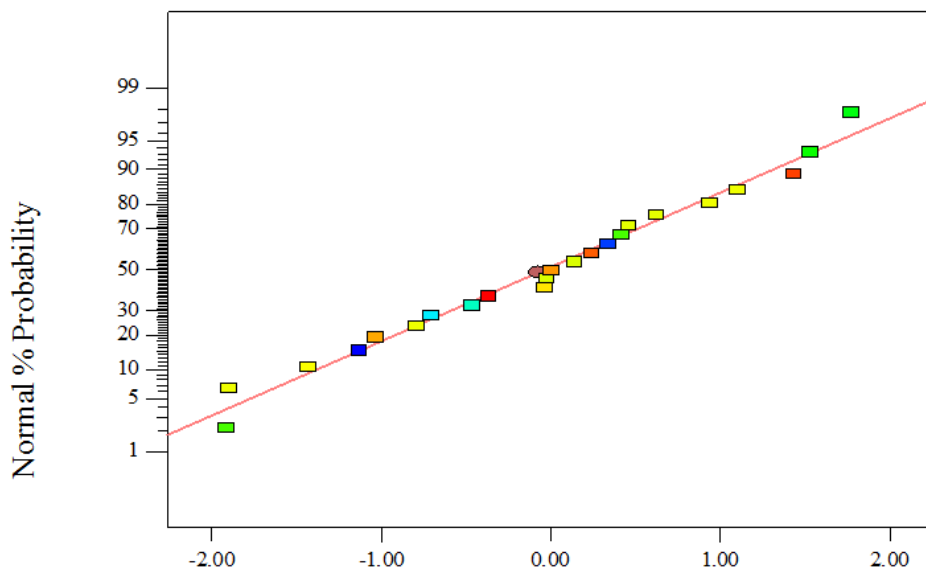
^b Degree of Freedom

^c Mean Square

The ANOVA for the yield of reaction is shown in Table 4. The model revealed that linear terms of A, B, and C, and quadratic terms of A², B², and C², and interaction term of AC had significant effect on yield of reaction with p-values lower than 0.05. The adequacy of the second-order response surface model was tested by the lack of fit (LOF) F-value, in which the residual error was compared with the pure error, and it demonstrated that the LOF was not significant. It means that the LOF was not important relative to the pure error. The model F-value of 270.0 showed that the presented model was acceptable and significant. Based on the R² value, the variability in the data for yield of reaction was 99.55%. The predicted R² value of 0.9768 was in reasonable agreement with the adjusted R² value of 0.9918, so it implied that there was no chance for indicating the not significant terms in the model. As illustrated in Fig. 1, the normal probability plot of studentized residuals shows that the errors are constant and normally distributed with the mean zero.

The response surface diagrams were plotted based on the proposed model to study the factor effects and their interactions on yield of reaction. The response surface plots visually showed the effects and interactions of the two experimental factors on the responses, while the other factors were kept constant at the center point. As illustrated in Fig. 2 (a, b), with increasing of catalyst amount up to 0.05 g the yield of reaction was increased because there existed more H⁺ in order to activate the carbonyl group of β-Ketoester. Since the yield was nearly

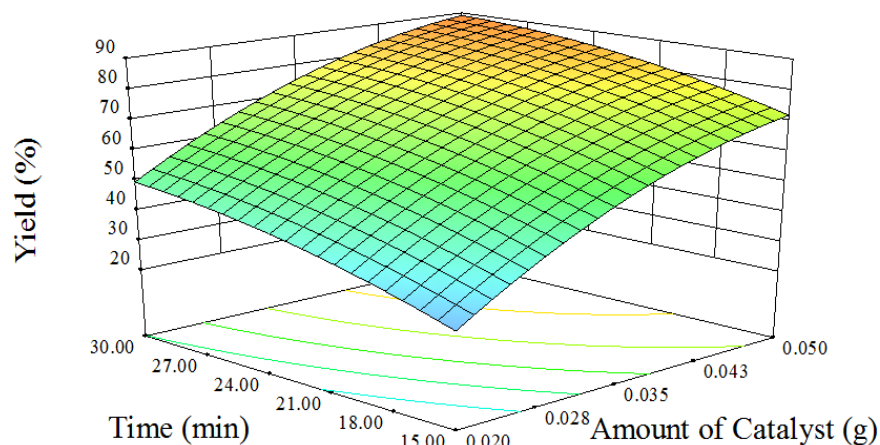
constant at the catalyst amount of higher than 0.05 g (Table 3, entry 21), there is no need to use higher amounts of catalyst.



Internally Studentized Residuals

Figure 1: Normal probability plots of studentized residuals for the refined quadratic model of reaction yield

The temperature of reaction plays an important role in yield, and the reaction was investigated in the temperature range of 65-85 °C. Fig. 2 (b, c) shows that the higher reaction temperature is better to reach the maximum yield. Therefore, the temperature of 85 °C was selected because the higher temperature had no significant effect on yield (Table 3, entry 23). As can be seen from Fig. 2 (a, c), the yield of reaction was increased with increasing of reaction time up to 30 min, however time values higher than 25 min had no considerable effect on yield. Finally, the non-linear Nelder–Mead optimization was carried out by using Design-Expert 8 trial version software, and the defined optimum condition for maximum reaction yield using the proposed catalyst was as follows: catalyst amount of 0.05 g, temperature of 85 °C, and time of 30 min. Under the optimal condition, the optimum predicted reaction yield with 95% confidence level was $98.5 \pm 2.4\%$. The validation of the predicted yield was achieved by performing



(a)

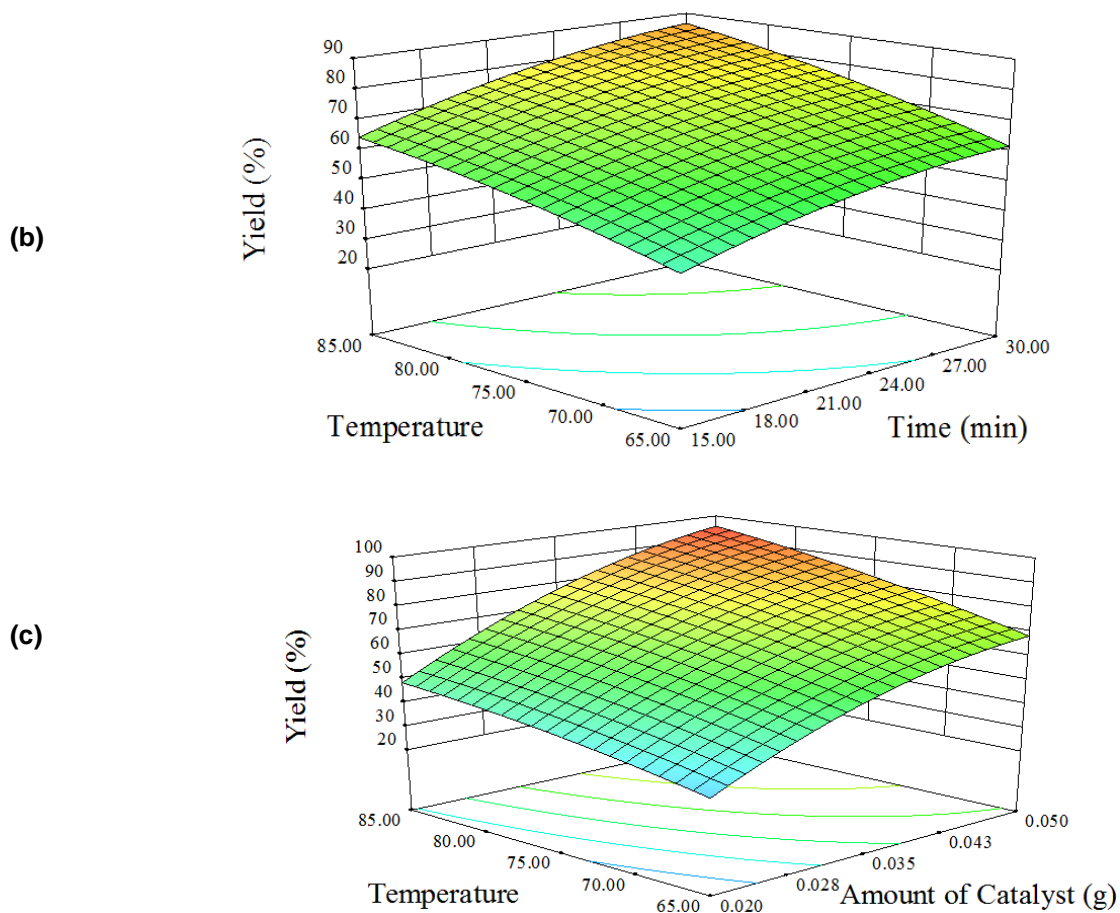


Figure 2: Response surface graphical representation of the reaction yield versus: (a) amount of catalyst – time; (b) amount of catalyst – temperature; (c) time – temperature.

Experiments under the optimized condition. The experimental reaction yield was found to be $98.0 \pm 4.1\%$, and it was in close agreement with the CCD model prediction.

Performance of proposed catalyst

The efficiency of acid modified bentonite catalyst was demonstrated by synthesizing dozen of coumarins using a series of monohydric and polyhydric phenols with β -keto esters (Table 5) under the optimum conditions. The proposed catalyst was found to be equally effective for reactions of phenols bearing either electron-donating (Table 5, entries 4-7) or electron-withdrawing substituents with β -keto esters (Table 5, entry 8). The present method is superior to previously reported methods regarding yields and reaction time [13, 15].

In Table 6, the ability to perform of our method for the synthesis of coumarin is compared with some other published works in literature. The reaction of resorcinol with ethyl acetoacetate was used as a model reaction. Each of these reported methods have their own advantages, but they often suffer from some drawbacks, including the use of organic solvent, (entry 6), longer reaction times (entries 1 –8), and moisture sensitive (entry 4). Recently we applied (Carboxy-3-oxopropylamino)-3-propylsilylcellulose (COPAPSC) as catalyst for the synthesis of coumarin derivatives by cyclo-condensation reaction of phenolic substrates with β -ketoesters [39]. Acid modified bentonite catalyst was inert, economical, and scalable.

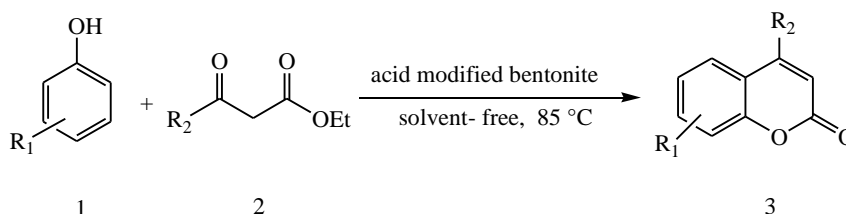


Table 5: Synthesis of coumarins via Pechmann condensations of phenols with ethyl acetoacetate by acidic modified bentonite^a.

Entry	R ₁	R ₂	Product	Time (min)	M.P. (°C)		Yield(%) ^b
					This work	lit. [ref.]	
1	3-OH	CH ₃	3a	30	183	185-187 [16]	94
2	2,6-(OH) ₂	CH ₃	3b	20	238-240	236-239 [16]	92
3	3,5-(OH) ₂	CH ₃	3c	20	280-282	281-283 [16]	93
4	3-Me-5-OH	CH ₃	3d	40	255-258	256-258 [16]	92
5	2-Me-3-OH	CH ₃	3e	45	264-267	263-265 [17]	93
6	3-MeO	CH ₃	3f	60	158-160	160-162 [16]	87
7	6-MeO-3-OH	CH ₃	3g	60	158-161	163-164 [16]	90
8	4-NO ₂	CH ₃	3h	60	147-149	151-154 [16]	85
9	3,5-(OH) ₂	CF ₃	3j	20	251-253	250-252 [13]	94
10	3-OH-4-Cl	CH ₃	3k	90	285-288	285-286 [11]	90
11	1-naphthol	CH ₃	3m	120	155-157	154-156 [16]	88

^a Reactions were performed with phenol (1.0 mmol), β-keto-ester (1.0 mmol), and acid modified bentonite (0.05 g) as catalyst at

85 °C under solvent-free conditions.

^b Isolated yields of pure products.

Reusability of proposed catalyst

After the completion of the first run to afford the corresponding coumarin in 94% yield (after purification), the catalyst was thoroughly washed with EtOH and diethyl ether and finally dried at 80 °C for 4 h. A new reaction was designed with fresh resorsinol and ethyl acetoacetate as reactants under the same reaction conditions. The recovered catalyst was successfully used in 5 consecutive runs, exhibiting consistent activity to afford an average yield of 88% with virtually no significant loss of performance. The results with the recyclable acid modified bentonite are summarized in Fig. 3.

Table 6. Comparison of results using acidic modified bentonite with results obtained by other works for the synthesis of 3a.

Entry	Catalyst	Reaction condition	Yield (%)	Ref.
1	Zr-TMS-TFA-25	Solvent-free, 100 °C, 9 h	90	40
2	PVPP-Bf ₃	EtOH, reflux, 2 h	91	41
3	Polyaniline-sulfate salts	Solvent-free, 150 °C, 6 h	70	26
4	nano-crystalline sulfated-zirconia	Solvent-free, 170 °C, 3 h	78	25
5	Mesoporous zirconium phosphate	Solvent-free, 150 °C, 4 h	76	27
6	Montmorillonite Clay	Toluene, reflux, 8 h	94	19
7	PW/Al-MCM-41	Solvent-free, 150 °C, 6 h	80	23
8	FeCl ₃ in ILs	[BMIM][Tf ₂ N], 70°C, 12 h	85	13
9	silica supported perchloric acid	Solvent-free, 130 °C, 35 min	95	22
10	ZrCl ₄	Solvent-free, 70 °C, 8 min	95	14
11	COPAPSC	Solvent-free, 85 °C, 30 min	94	39
12	Acidic modified bentonite	Solvent-free, 85 °C, 30 min	94	This work

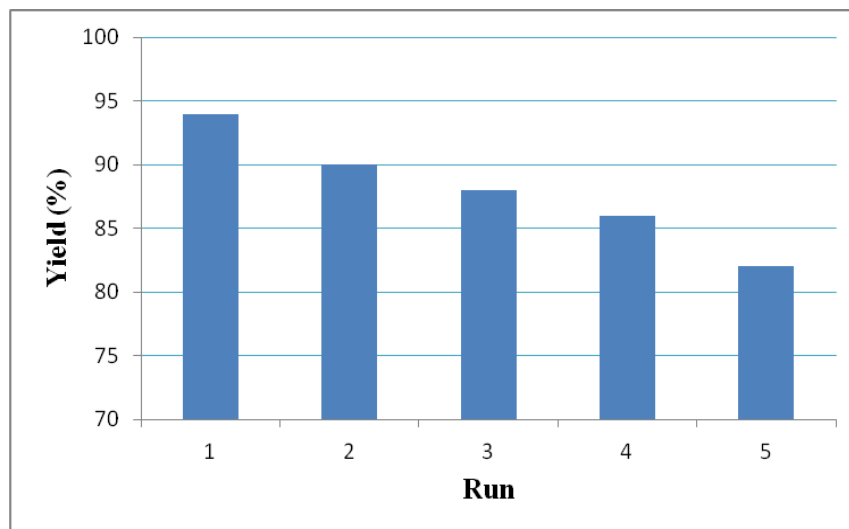


Figure 3: Reusability of acid activated bentonite in cyclo-condensation of resorcinol and ethylacetoacetate at 85 °C under solvent-free conditions in 30 min.

CONCLUSIONS

We have implemented an acid modified bentonite as an efficient, reusable, green, and solidly supportive acid catalyst for the synthesis of coumarine derivatives by cyclocondensation reaction of phenolic substrates with β - ketoesters. The broad scope, operational simplicity, and practicability render it as an attractive approach for producing of different coumarine derivatives with potential use in biologically important compounds.

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REFERENCES

- A. Mohammadinezhad, M.A. Nasser, M. Salimi, *RSC Adv.*, 2014, 4, 39870–39874.
A. S., Özcan, A. Özcan, *J. Colloid. Interface. Sci.*, 2004, 276, 39–46.
A. Sinhamahapatra, N. Sutradhar, S. Pahari, H.C. Bajaj, A. B. Panda, *Applied Catalysis A: General*, 2011, 394, 93–100.
B. Karimi, H. Behzadnia, *Catal. Commun.*, 2011, 12, 1432–1436.
B. Tyagi, M.K. Mishra, R.V. Jasra, *J. Mol. Catal. A: Chem.*, 2007, 276, 47–56.
E. Eren, B. Afsin, *J. Hazard. Mater.*, 2009, 166, 830–835.
E. Galan, *Clay Miner.*, 1996, 31, 443–453.
E.V.O. John, S.S. Israelstam, *J. Org. Chem.*, 1961, 26, 240–242.
F., Bergaya, G. Lagaly, *Applied Clay Science*, 2001, 19, 1–3.
F.W. Canter, F.H. Curd, A. Robertson, *J. Chem. Soc. CLXVI.-Hydroxy-carbonyl compounds, Part III*, 1931, 1255–1265.
G. Brufola, F. Fringuelli, O. Piematti, F. Pizzo, *Heterocycles*, 1996, 43, 1257–1266.
G. Cavettos, G.M. Nano, G. Palmisano, S. Tagliapietra, *Tetrahedron: Asymmetry* 2001, 12, 707–709.
G. Smith, Ch. S. Reddy, *Synth. Commun.*, 2004, 34, 3997–4003.
I. Yavari, R. R. Hekmat-shoa, A. Zonouzi, *Tetrahedron Lett.*, 1998, 39, 2391–2392.
J.R. Johnson, *Org. React.*, 1942, 1, 210–265.
L.L. Woods, J. Sapp, *J. Org. Chem.*, 1962, 27, 3703–3705.
M. Mokhtary, F. Najafzadeh, *C.R. Chimie*, 2012, 15, 530–532.
M. Salimi, *J. Iran. Chem. Soc.*, 2016, 4, 295–308.
M. Salimi, M.A. Nasser, T. Daliran Chapesshloo, B. Zakerinasab, *RSC Adv.*, 2015, 5, 33974–33980.
M.A. Nasser, A. Mohammadinezhad, M. Salimi *J. Iran. Chem. Soc.*, 2015, 12, 81–86.

- M.A. Nasser, M. Salimi, A.A. Esmaeili, RSC Adv., 2014, 4, 61193–61199.
M.A. Nasser, M. Salimi, Letters in Organic Chemistry, 2013, 10, 164-170.
M.C. Laufer, H. Hausmann, W.F. Hölderich, J. Catal., 2003, 218, 315–320.
N.Cairns, M. L. Harwood, D.P Astles, J. Chem. Soc. Perkin Trans, 1994, 1, 3101-3107.
P. Kalita, R. Kumar, Microporous and Mesoporous Materials, 2012, 149, 1–9.
R. Sabou, W.F. Hoelderich, D. Ramprasad, R. Weinand, J. Catal., 2005, 232, 34–37.
R.L Shriner, Org. React., 1942, 1, 1-37.
R.O. Kennedy, R.D. Thornes, Coumarins: Biology, Applications and Mode of Action, John Wiley and Sons, Chichester, 1997.
S. Palaniappan, R. C. Shekhar, J. Mol. Catal. A: Chem., 2004, 209, 117–124.
S. S. Bahekar, D. B. Shinde, Tetrahedron Lett., 2005, 46, 6957–6959.
S. Selvakumar, M. Chidambaram, A.P. Singh, Catal. Commun., 2007, 8, 777–783.
S. Sudha, K. Venkatachalam, S. Vishnu Priya, J. Herbert Mabel, M. Palanichamy, V. Murugesan, J. Mol. Catal. A: Chem., 2008, 291, 22–29.
S.E. Garc'ia-Garrido, J. Francos, V. Cadierno, J.M. Basset V. Polshettiwar, Chem. Sus. Chem., 2011, 4, 104–111.
S.K. De, R.A. Gibbs, Synthesis, 2005, 8, 1231–1233.
S.M. Sethna, N. M. Shah, Chem. Rev. 1945, 36, 1–62.
T.S. Li, Z.H. Zhang, F. Yang, C.G. Fu, J. Chem. Res., 1998, 38–39.
V. Kumar, S. Tomar, R. Patel, A. Yousaf, V. S. Parmar, S. V. Malhotra, Synth. Commun., 2008, 38, 2646–2654.
V. M. Alexander, R. P. Bhat, S. D. Samant, Tetrahedron Lett., 2004, 45, 7999–8001.
V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.M. Basset, Chem. Rev., 2011, 111, 3036–3075.
V.H Pechmann, C. Duisberg, Chem. Ber., 1884, 17, 929-979.
X.T. Liang, W.S. Fang, Medicinal chemistry of bioactive natural products, John Wiley & Sons: Hoboken, New Jersey, 2006.