RESEARCH PAPER

Nano-kaolin/Ti(IV)/Fe_3O_4: a Natural Based Magnetic Nano-catalyst for the Synthesis of Coumarins

Bi Bi Fatemeh Mirjalili [1]*, Roya Soltani [1] and Abdolhamid Bamoniri [2]

[1] *Department of Chemistry, College of Science, Yazd University, Yazd, I.R.Iran*

[2] *Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R.Iran*

ARTICLE INFO

Article History:
Received 12 January 2021
Accepted 19 March 2021
Published 01 April 2021

Keywords:
Coumarine
Magnetic nano-catalyst
Nano-kaolin/Ti(IV)/Fe_3O_4
Solvent free condition

ABSTRACT

Nano-kaolin/Ti(IV)/Fe_3O_4 as an efficient natural based magnetic nano-catalyst was synthesized and characterized using commercial nano-kaoline. Structural properties of this catalyst were investigated by using various techniques such as fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM), thermal gravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDX). Coumarines have shown various biological activities such as analgesic, antimicrobial, antimalarial, antioxidant, anti-inflammatory, anticancer, antituberculosis and anti-HIV properties. Nano-kaolin/Ti(IV)/Fe_3O_4 was used for the synthesis of coumarines via Pechmann condensation between phenols and β-ketoester under solvent-free conditions at 120 °C. In this procedure, we have used phloroglucinol, resorcinol, 1-naphthol, pyrogalol and chatechol as nucleophile and ethyl acetoacetate, ethyl 2-chloro-acetoacetate, ethyl propionylacetate, ethyl 3-oxo-hexanoate, 2-ethoxycarbonyl cyclopentanone and ethyl benzoylacetate as electrophile. The structure of coumarine products was identified by FTIR and NMR spectroscopies. This method offers has several advantages such as easy workup, short reaction times, high product yields and reusability of catalyst.

How to cite this article
Mirjalili B. F, Soltani R and Bamoniri A. Nano-kaolin/Ti(IV)/Fe_3O_4: a Natural Based Magnetic Nano-catalyst for the Synthesis of Coumarins. J Nanostruct, 2021; 11(2):243-251. DOI: 10.22052/JNS.2021.02.005

INTRODUCTION

Coumarin is a heterocyclic compound that plays an important role in the field of natural products and synthetic organic chemistry [1]. Coumarins are also a member of the benzopyrone family [2]. These compounds have shown various biological activities such as analgesic, antimicrobial, antimalarial, antioxidant, anti-inflammatory, anticancer, antituberculosis and anti-HIV properties [3]. In addition, coumarins are used in various industries such as perfumery, cosmetics, food industry and dispersed fluorescent and laser dyes [4-6]. Coumarins are synthesized in several various methods, such as Reformatsky [7], Wittig [8-9], Knoevenagel [10-11], Perkin [12], and Pechmann reaction [13]. One of the widely used methods for the synthesis of coumarin is the Pechmann reaction, which involves the condensation reaction between phenols and β-ketoesters by various types of acidic catalyst [14-15]. The catalysts including H_2SO_4 [13], P_2O_5 [16-17], $AlCl_3$ [18], CF_3COOH [19], starch-SO_3H [20], $SnCl_4$-SiO_2 [21], $NbCl_5$ [22], Nano-$CuFe_2O_4$ [23], $ZrCl_4$ [24], $[Et_3NH]^+[HSO4]^-$ [25] and $[Hmim]^+[HO_3SCH_2SO_3]^-$

* *Corresponding Author Email: fmirjalili@yazd.ac.ir*

[26] have been applied for the preparation of these compounds. The drawbacks of these protocols are high price of catalyst, long reaction time and required large amounts of catalyst, which lead to environmental pollution.

Kaolin is a clay mineral, part of the group of industrial minerals with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6) octahedral [27-29]. The various physical attributes of kaolin mineral have made it useful in various ways industrially and these include paints, ceramics, rubber, paper, medicine, petroleum and glass industries [30]. One of main usege of kaolin is catalyst role in the chemical industry [31]. Magnetic nanoparticles are a category of nanoparticle that can be manipulated using magnetic fields. Such particles generally include of two components, a magnetic material, often iron, nickel and cobalt, and a chemical component that has functionality [32-34]. Among them, magnetic nanoparticles (Fe_3O_4) have been the focus of much research recently because advantages such as high stability, low toxicity and easy separation from reaction media [35]. In this work, we wish to report application of nano-kaolin/Ti(IV)/Fe_3O_4 [28] for synthesis of coumarines via pechmann reaction include of the condensation reaction of β-keto esters with phenols.

MATERIALS AND METHODS

All compounds were purchased from Merck, Aldrich and Fluka chemical companies and used without any additional purification. FT-IR spectra were run on a Bruker, Equinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the NMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

Preparation of Fe_3O_4 NPs

A mixture of $FeCl_3.6H_2O$ (2.7 g, 10 mmol) and $FeCl_2.4H_2O$ (1 g, 5 mmol) in deionized water (25 mL) was warmed until 80 °C. Then 17 ml of NH3 (30%) was added slowly and the mixture was stirred with mechanical stirrer for 30 minutes. Then black magnetic nanoparticles were collected by using an external magnet and washed three times with deionized water. Finally Fe_3O_4 NPs were dried at 80 °C for 4 hours.

Preparation of nano-kaolin/Ti(IV)

At first, 1 ml of $TiCl_4$ was added drop wise to a mixture of nano-kaolin (2 g) in 10 ml of dichloromethane In a beaker. the mixture stirred by using a mechanical stirrer for 1 h at room temperature. The resulting suspension was filtered and washed with dichloromethane and dried at room temperature.

Preparation of nano-kaolin/Ti(IV)/Fe_3O_4

the mixture of nano-kaolin/Ti(IV) (2 g) and dichloromethane (10 mL) were dispersed in the ultrasonic irradiation bath for 30 minutes. Then, nano-Fe_3O_4 (1 g) was added to the mixture. Again, compound placed for 40 minutes in the ultrasonic irradiation bath to disperse the particles. The resulting suspension was collected by using external magnet and washed with dichloromethane and dried at room temperature.

General procedure for the synthesis of coumarines

The mixture of phenol (1 mmol), ethyl acetoacetate (1 mmol) and nano-kaolin/Ti(IV)/Fe_3O_4 (0.03 g) was warmed at 100 ºC In a sand bath and stirred by using a mechanical stirring motor with a speed of 50 rpm . The advance of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was dissolved in ethanol and the catalyst was separated by an external magnet. Finally, The reaction mixture was were purified using column chromatography on silica gel and recrystallized from hot ethanol to afford pure coumarin derivatives.

RESULTS AND DISCUSSION

Nano-kaolin/Ti(IV)/Fe_3O_4 was generally prepared as a magnetic nano-catalyst in two-steps process. At first, $TiCl_4$ was added to the mixture of nano-Kaolin and CH_2Cl_2. The resulted white powder (nano-kaolin/Ti(IV)) was added to the suspension of nano Fe_3O_4 in CH_2Cl_2 under ultrasonic condition to formation of nano-kaolin/Ti(IV)/Fe_3O_4 as a brown magnetic powder.

The particles size of the nano-kaolin/Ti^{4+}/Fe_3O_4 was studied using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) and were less than 100 nm (Fig. 1).

Energy-dispersive X-ray spectroscopy (EDS) was used to determine the percentage of elements in the nano-kaolin/Ti^{4+}/Fe_3O_4. (Fig. 2) The percentage of Fe, Si, Al, Ti, Cl, O and K in nano-kaolin/Ti^{4+}/Fe_3O_4 was 37.4, 25.5, 12.6, 11.0, 8.2, 4.2 and 1.2

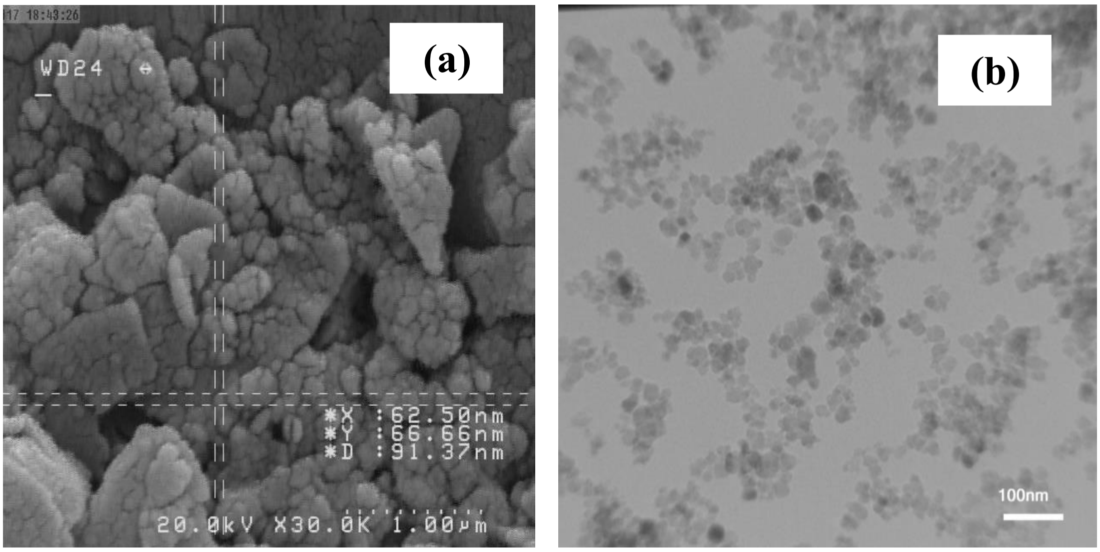


Fig. 1. (a) FESEM and (b) TEM images of nano-kaolin/Ti^{4+}/Fe_3O_4.

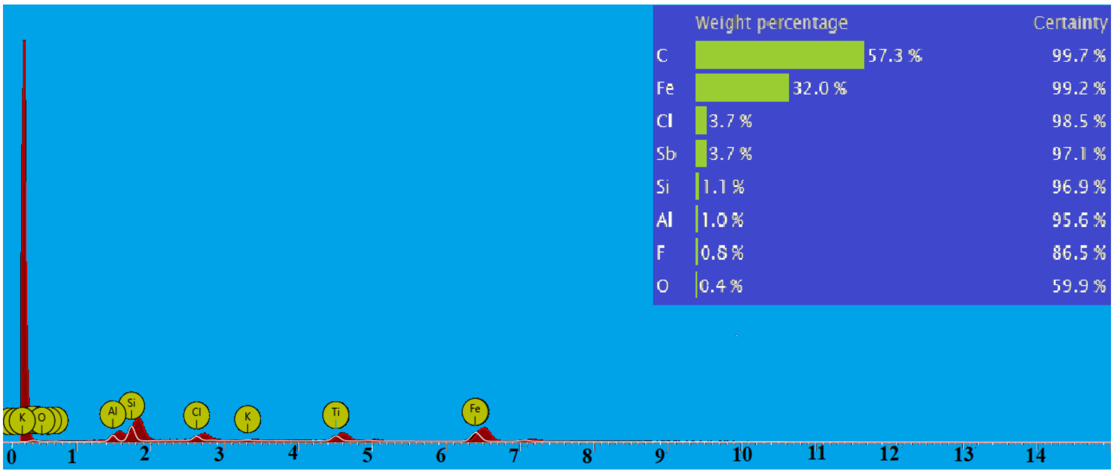


Fig. 2. The EDX spectra of nano-kaolin/Ti^{4+}/Fe_3O_4

respectively.

The thermal stability (TG–DTA) of nano-kaolin/Ti^{4+}/Fe_3O_4 was studied by thermo-gravimetric analysis (TGA) in a temperature range of 50-800 °C (Fig. 3). According to the figure 4, at 100-250 ºC, 4% of catalyst weight was reduced, which can be related to the removal of moisture and bonded water. Also, the catalyst has lost 80% of its weight in the range of 250-600 ºC probably due to collapse of the Kaolin network. According to the TGA curve, this catalyst is stable to 230 °C and is suitable for reactions that were carried out at temperatures below 230 °C.

The vibrating sample magnetometer (VSM) pattern of catalyst at room temperature shows, the coercivity value is zero and there was no hysteresis loop and remanence that confirm the catalytic superparamagnetic property (Fig. 4). The saturation magnetization (Ms) values of Fe_3O_4 and the nano-kaolin/Ti^{4+}/Fe_3O_4 were 50 and 23 emu g^{-1}, respectively. Although the magnetization of catalyst is lower than Fe_3O_4, the catalyst can be easily separated from the solution with an external magnet.

The X-ray diffraction (XRD) of nano-kaolin/Ti^{4+}/Fe_3O_4 is shown in Figure 5. According to the XRD pattern, signals at 2θ equal to 13º, 20º, 25º, 41º, 46º, 61º and 68º indicates the presence of

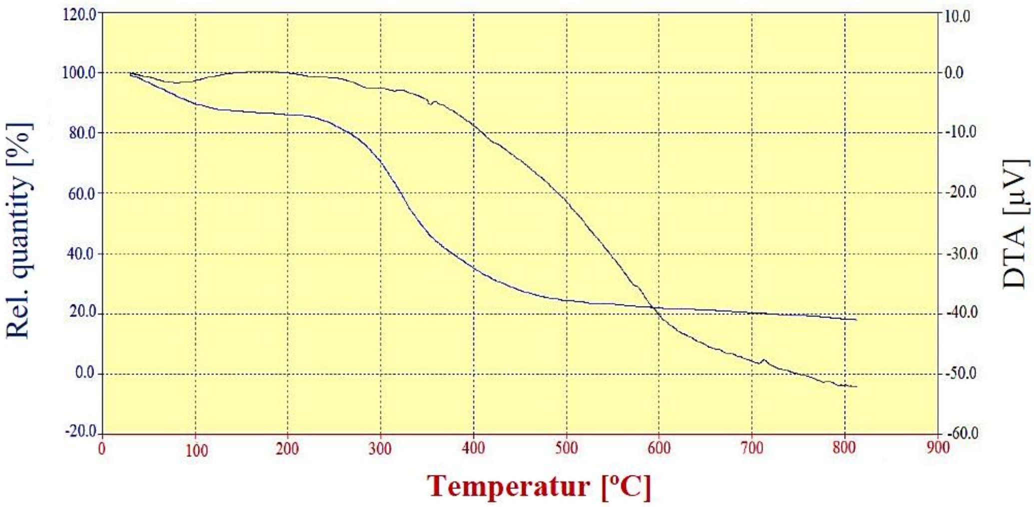


Fig. 3. Thermal gravimetric analysis of nano-kaolin/Ti^{4+}/Fe_3O_4

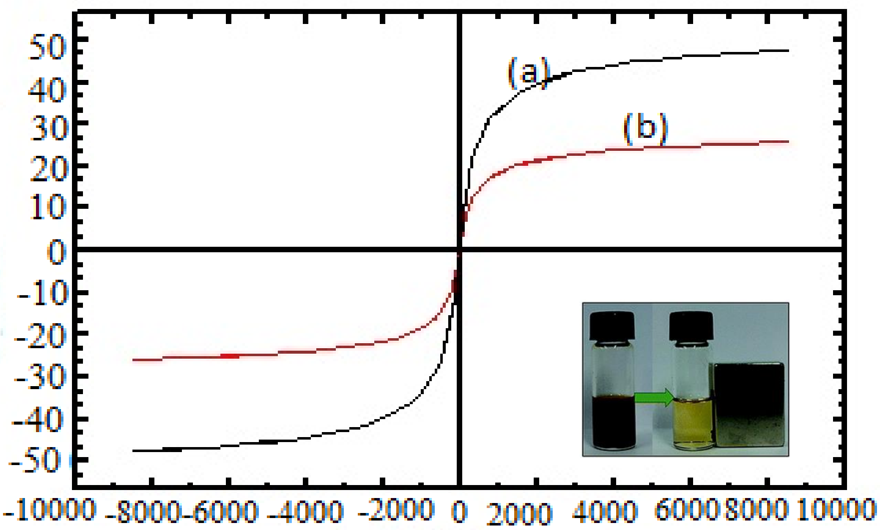


Fig. 4. Magnetization loops of (a) Fe_3O_4 and (b) nano-kaolin/Ti^{4+}/Fe_3O_4

kaolin. The four signals in 2θ = 21º, 27º, 39º and 50º show the existence of SiO_2. Also, the signals in 2θ =31º, 36º, 44º, 58º and 63º are related to Fe_3O_4. Presumably, three other peaks in 2θ of 37°, 43° and 55° revealed that Ti was bonded to Kaolin and Fe_3O_4.

After characterization of nano-kaolin/Ti(IV)/Fe_3O_4, its catalytic activity was investigated for the synthesis of coumarin derivatives by using Pechmann condensation between phenols and β-ketoester. To select optimization conditions, the reaction of ethyl acetoacetate and resorcinol as a model reaction was studied in various conditions. As shown in Table 1, entry 14, the best conditions for the synthesis of coumarines under solvent-free conditions are using 0.03 g of catalyst at 120 °C.

With the optimized reaction conditions for the model reaction, 7-hydroxy-2H-chromen-2-one derivatives were explored by the reaction of phenolic derivatives with a range of β-ketoester and the results are summarized in Table 1. The nature of the substituent on β-ketoester and phenols have a considerable effect on the time and yield of the reaction. β-Ketoesters with electron withdrawing group and phenol with electron releasing group reacts in shorter time with higher

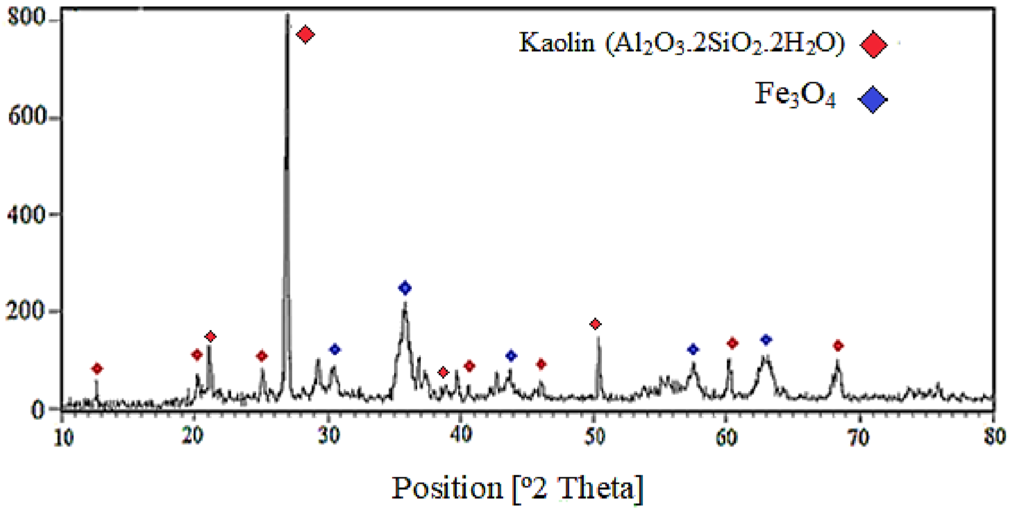
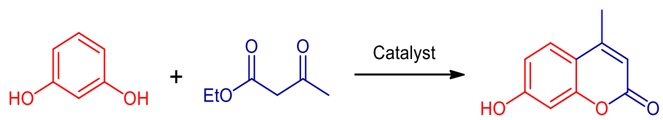


Fig. 5. XRD pattern of nano-kaolin/Ti^{4+}/Fe_3O_4

Table 1. The reaction of ethyl acetoacetate and resorcinol in the presence of nano-kaolin/Ti(IV)/Fe_3O_4 under different conditions[a]



Entry	Catalyst (g)	Solvent/ Condition	Time (h)	Yield (%)[b]
1	Fe_3O_4 (0.03)	-/120 ºC	1.5	**40**
2	Kaolin (0.03)	-/120 ºC	3	**50**
3	Nano-Kaolin/Ti(Ⅳ) (0.03)	-/120 ºC	1	**70**
4	Catalyst[c] (0.03)	H_2O/Reflux	6	**65**
5	Catalyst[c] (0.03)	C_2H_5OH/Reflux	10	**0**
6	Catalyst[c] (0.03)	H_2O/120 ºC	10	**0**
7	Catalyst[c] (0.03)	PEG-100/ultrasonic irradiation	1	**0**
8	Catalyst[c] (0.03)	H_2O/ microwave	15(min)	**45**
9	Catalyst[c] (0.03)	-/90 ºC	1.5	**65**
10	Catalyst[c] (0.03)	-/100 ºC	1.5	**68**
11	Catalyst[c] (0.03)	-/110 ºC	1.5	**70**
12	Catalyst[c] (0.03)	-/120 ºC	1.5	**94**
13	Catalyst[c] (0.03)	-/120 ºC	1.5	**90**
14	Catalyst[c] (0.02)	-/120 ºC	1.5	**70**
15	Catalyst[c] (0.04)	-/120 ºC	1.5	**65**
16	Catalyst[c] (0.05)	-/120 ºC	1.5	**70**
17	Catalyst[c] (0.03), 2[th]run	-/120 ºC	1.5	**90**
18	Catalyst[c] (0.03), 3[th]run	-/120 ºC	1.5	**86**
19	Catalyst[c] (0.03), 4[th]run	-/120 ºC	1.5	**81**

[a]The amount ratios of resorcinol (mmol) and ethyl acetoacetate (mmol) are equal to 1:1
[b]Isolated yield
[c]Nano-kaolin/Ti(IV)/Fe_3O_4

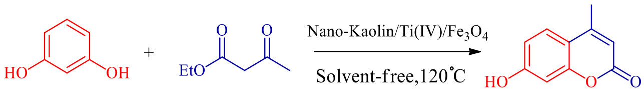
yield. The product structure were characterized by using melting point, FT-IR, and ^{1}H-NMR spectra.

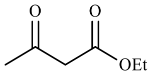
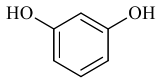
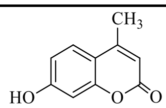
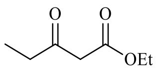
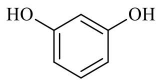
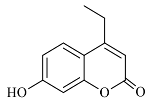
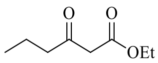
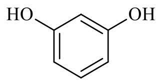
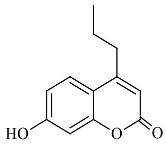
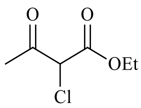
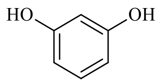
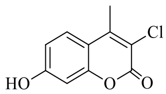
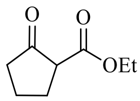
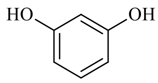
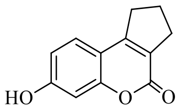
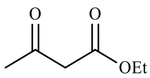
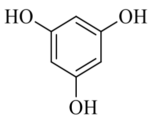
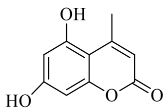
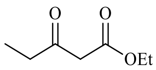
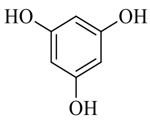
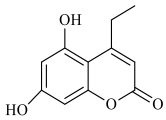
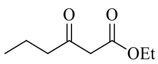
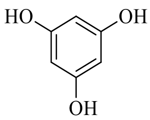
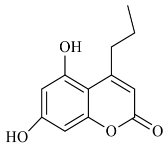
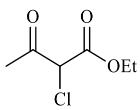
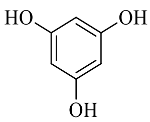
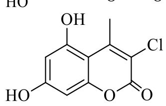
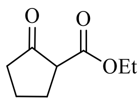
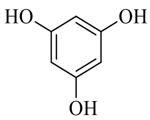
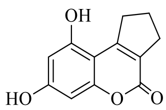
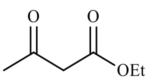
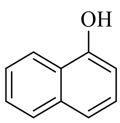
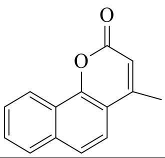
The reusability of the catalyst was also investigated on the model reaction in the presence of nano-kaolin/Ti(IV)/Fe_3O_4 at 120 ºC under solvent-free conditions. That way, catalyst was separated by using an external magnet, washing with ethanol and drying at room temperature. The results indicated that the catalyst nano-kaolin/Ti(IV)/Fe_3O_4 can be reused for four times without considerable loss at its catalytic activity (Table 1).

The suggested mechanism for the synthesis of coumarines is shown in Fig. 6. In this reaction, the Ti(IV) cation in catalyst doing as a Lewis acid and activates carbonyl groups in substrates.

The efficiency of nano-kaolin/Ti(IV)/Fe_3O_4

Table 2. The synthesis of coumarine derivatives[a]



Entry	R	Phenol	Product	Time (h)	Yield (%)[b]	Melting Point Observed	Melting Point Reported	Ref.
1				1.5	94	180-182	180-182	[20]
2				1.8	80	170-171	-	-
3				1	70	129-132	-	-
4				0.65	85	240-244	236-240	[36]
5				2.5	72	283-284	284-285	[37]
6				1	85	286-288	288-290	[38]
7				1.75	83	262-264	-	-
8				1	70	233-236	-	-
9				0.65	87	320-322	317-319	[36]
10				0.75	82	271-272	-	-
11				2	75	154-156	153-155	[38]

[a]One mmol of phenol and β-ketoester were used.
[b]Isolated yield

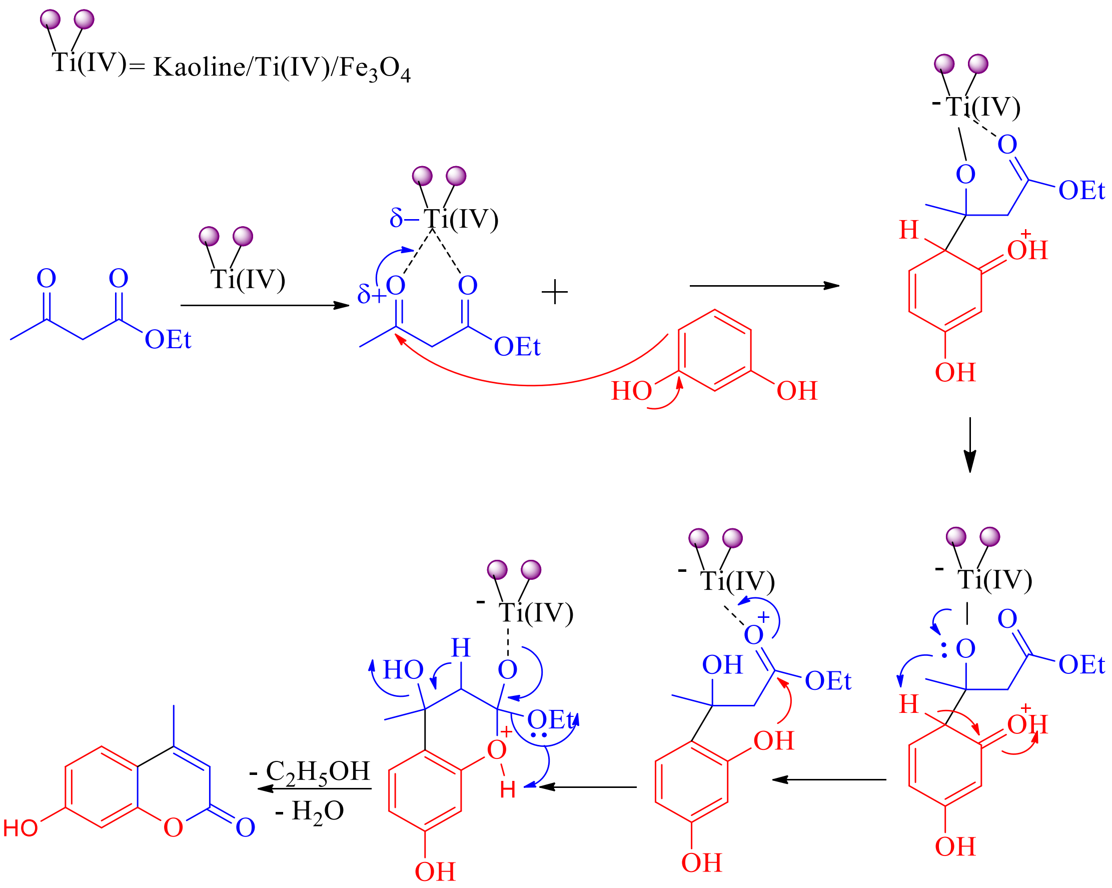


Fig. 6. A proposed mechanism for preparation of coumarine

Table 3. Comparison of nano-kaolin/Ti(IV)/Fe_3O_4 catalyst with other reported catalysts for the synthesis of 7-hydroxy-4-methyl-2*H*-chromen-2-one[a]

Entry	Catalyst	Solvent/Condition	Time(h)	Yield (%)[b, Ref.]
1	$In(OTf)_3$ (1 mol%)	–/ 120 ºC	0.53	87[37]
2	$SnCl_4$-SiO_2 (5 mol%)	–/ 120 ºC	0.58	90[21]
3	$[Et_3NH]^+[HSO_4]^-$ (0.04 g)	–/ 110 ºC	0.25	94[25]
4	$[Hmim]^+[HSO_3CH_2SO_3]^-$ (0.75mmol)	–/ 80 ºC	1	90[26]
5	Fe_3O_4@SiO_2@$PrSO_3H$ (0.018 g)	–/ 130 ºC	0.42	96[39]
6	Nanosilica molybdic acid (5 mol%)	–/ 80 ºC	0.33	93[40]
7	nano-kaolin/Ti(IV)/Fe_3O_4 (0.03 g)	–/ 120 ºC	1.5	94[This work]

[a] One mmol of any substrate (resorcinol and ethyl acetoacetate) were used.
[b]Isolated yield

catalyst in Pechmann reaction was compared with other reported ones (Table 3). The results shows, one of the best catalysts for the synthesis of coumarin in solvent-free conditions is nano-kaolin/Ti(IV)/Fe_3O_4 with short reaction time and high yield.

CONCLUSION

In conclusion, we have reported the preparation and description of nano-kaolin/Ti(IV)/Fe_3O_4 as an efficient and magnetically recyclable heterogeneous catalyst. This catalyst was applied to synthesize of coumarine derivatives via Pechmann condensation reaction of phenols and β-ketoester under solvent-free condition at 120 °C. Several main advantages of this protocol includes high yields, short reaction times, mild reaction conditions, simple work-up procedure and easy separation with reusability of the catalyst

Conflicts of interest

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

ACKNOWLEDGEMENTS

The Research Council of Yazd University is gratefully acknowledged for the financial support for this work.

REFERENCES

1. Singer LA, Kong NP. Vinyl Radicals. Stereoselectivity in Hydrogen Atom Transfer to Equilibrated Isomeric Vinyl Radicals1. Journal of the American Chemical Society. 1966;88(22):5213-9.
2. Shahrisa A, Zirak M, Mehdipour AR, Miri R. Synthesis and calcium channel antagonist activity of new symmetrical and asymmetrical 4-[2-chloro-2-(4-chloro-6-methyl-2-oxo-2H-pyran-3-yl)vinyl]-substituted 1,4-dihydropyridines. Chemistry of Heterocyclic Compounds. 2011;46(11):1354-63.
3. Kostova I, Momekov G, Zaharieva M, Karaivanova M. Cytotoxic activity of new lanthanum (III) complexes of bis-coumarins. European Journal of Medicinal Chemistry. 2005;40(6):542-51.
4.Kennedy O. Thornes RD. Clinical and Biological Observations Associated with Coumarins. Coumarins: Biology, Applications and Mode of Action. John Wiley & Sons, Inc., New York, NY. 1997;256.
5. Zahradnik M. The Production and Application of Fluorescent Brightening Agents. Wiley & Sons, 1992.
6. Murray RDH, Mendez J, Brown SA. The Natural Coumarins: Occurrence, Chemistry and Biochemistry. Wiley & Sons: Inc., New York, NY. 1982.
7. Shriner RL. Organic Reactions. Vol I, John Wiley and Sons: Inc., New York. 1942; 2-36.
8. Narasimahan NS, Mali RS, Barve MV. Synthesis 906. Tetrahedron Lett. 1979; 39: 2391.
9. Yavari I, Hekmat-Shoar R, Zonouzi A. A new and efficient route to 4-carboxymethylcoumarins mediated by vinyltriphenylphosphonium salt. Tetrahedron Letters. 1998;39(16):2391-2.
10. Fringuelli F, Brufola G, Piermatti O, Pizzo F. Simple and Efficient One-Pot Preparation of 3-Substituted Coumarins in Water. HETEROCYCLES. 1996;43(6):1257.
11.Jones G. The Koevenagel Condensation. Org. React.. 1967;15:204-599.
12.Johnson JR. The Perkin Reaction and Related Reactions. Org. React. 1942; 1: 210-265.
13. v. Pechmann H. Neue Bildungsweise der Cumarine. Synthese des Daphnetins. I. Berichte der deutschen chemischen Gesellschaft. 1884;17(1):929-36.
14.Sethna S, Phadke R. The Pechmann Reaction. Org. React. 1953; 7: 1-58.
15.Russell A, Frye JR. 2, 6-Dihydroxyacetophenone: Acetophenone,2,6-dihydroxy. Org. Synth. 1941; 21: 22.
16. Simonis H, Remmert P. Eine neue Flavon-Synthese. Berichte der deutschen chemischen Gesellschaft. 1914;47(2):2229-33.
17. Robertson A, Sandrock WF, Hendry CB. CCCXXX.—Hydroxy-carbonyl compounds. Part V. The preparation of coumarins and 1 : 4-pyrones from phenol, p-cresol, quinol, and α-naphthol. J Chem Soc. 1931;0(0):2426-32.
18. Sethna SM, Shah NM, Shah RC. 44. Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. Part I. The condensations of methyl β-resorcylate, β-resorcylic acid, and resacetophenone with ethyl acetoacetate. J Chem Soc. 1938;0(0):228-32.
19. Woods LL, Sapp J. A New One-Step Synthesis of Substituted Coumarins. The Journal of Organic Chemistry. 1962;27(10):3703-5.
20.Rezaei R, Farjam MH, Farasat M. Coumarin Synthesis via Pechmann Condensation Utilizing Starch Sulfuric Acid as a Green and Efficient Catalyst Under Solvent-Free Conditions. Org. Chem.: An Indian J. 2014; 10(2): 73-78.
21. Sun R, Gao Y, Ma Y, Yang G, Li Y. SnCl4 grafted on silica gel: an efficient catalyst for solvent-free synthesis of coumarins via the Pechmann condensation. Journal of the Iranian Chemical Society. 2016;14(3):737-42.
22. Gao S-T, Li C, Wang Y, Ma J-J, Wang C, Zhang J-W. NbCl5-Catalyzed, Solvent-Free, One-Pot Synthesis of Coumarins. Synthetic Communications. 2011;41(10):1486-91.
23. Baghbanian SM, Farhang M. CuFe2O4 Nanoparticles: A Magnetically Recoverable and Reusable Catalyst for the Synthesis of Coumarins via Pechmann Reaction in Water. Synthetic Communications. 2013;44(5):697-706.
24. Smitha G, Sanjeeva Reddy C. ZrCl4-Catalyzed Pechmann Reaction: Synthesis of Coumarins Under Solvent-Free Conditions. Synthetic Communications. 2004;34(21):3997-4003.
25. Karimi-Jaberi Z, Masoudi B, Rahmani A, Alborzi K. Triethylammonium Hydrogen Sulfate [Et3NH][HSO4] as an Efficient Ionic Liquid Catalyst for the Synthesis of Coumarin Derivatives. Polycyclic Aromatic Compounds. 2017;40(1):99-107.
26. Song D, Chen J, Liang Y-M. Anionic SO3H-functionalized ionic liquid: An efficient and recyclable catalyst for the Pechmann reaction of phenols with ethyl acetoacetate. Synthetic Communications. 2018;48(6):692-8.
27. Bish DL. Rietveld Refinement of the Kaolinite Structure at 1.5 K. Clays and Clay Minerals. 1993;41(6):738-44.
28. Mirjalili BBF, Soltani R. Nano-kaolin/Ti4+/Fe3O4: a magnetic reusable nano-catalyst for the synthesis of pyrimido[2,1-b] benzothiazoles. RSC Advances. 2019;9(33):18720-7.
29. Du C, Yang H. Investigation of the physicochemical aspects from natural kaolin to Al-MCM-41 mesoporous materials. Journal of Colloid and Interface Science. 2012;369(1):216-22.
30. Murray HH. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. Applied Clay Science. 2000;17(5-6):207-21.
31. Doyle AM, Albayati TM, Abbas AS, Alismaeel ZT. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. Renewable Energy. 2016;97:19-23.
32. Yu WW, Falkner JC, Yavuz CT, Colvin VL. Synthesis of monodisperse iron oxide nanocrystals by thermal decomposition of iron carboxylate salts. Chemical Communications. 2004(20):2306.
33.Zhao SY, Lee DG, Kim CW, Cha HG, Kim YH, Kang YS. Synthesis of Magnetic Nanoparticles of Fe_3O_4 and $CoFe_2O_4$ and their Surface Modification by Surfactant Adsorption. Bull. Korean Chem. Soc. 2006; 27(2): 237-242.
34. Chen M, Kim J, Liu JP, Fan H, Sun S. Synthesis of FePt Nano-

cubes and Their Oriented Self-Assembly. Journal of the American Chemical Society. 2006;128(22):7132-3.
35. Lu A-H, Salabas EL, Schüth F. Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application. Angewandte Chemie International Edition. 2007;46(8):1222-44.
36. Rodríguez-Domínguez JC, Kirsch G. Sulfated zirconia, a mild alternative to mineral acids in the synthesis of hydroxycoumarins. Tetrahedron Letters. 2006;47(19):3279-81.
37. Abbasi Z, Rezayati S, Bagheri M, Hajinasiri R. Preparation of a novel, efficient, and recyclable magnetic catalyst, γ -Fe 2 O 3 @HAp-Ag nanoparticles, and a solvent- and halogen-free protocol for the synthesis of coumarin derivatives. Chinese Chemical Letters. 2017;28(1):75-82.
38. Karami B, Kiani M, Hoseini MA. In(OTf)3 as a powerful and recyclable catalyst for Pechmann condensation without solvent. Chinese Journal of Catalysis. 2014;35(7):1206-11.
39. Esfahani FK, Zareyee D, Yousefi R. Sulfonated Core-Shell Magnetic Nanoparticle (Fe3O4@SiO2@PrSO3H) as a Highly Active and Durable Protonic Acid Catalyst; Synthesis of Coumarin Derivatives through Pechmann Reaction. ChemCatChem. 2014;6(12):3333-7.
40. Kiani M, Karami B. Nanosilica molybdic acid: synthesis, characterization and application as a green and reusable catalyst for the Pechmann condensation. Journal of the Iranian Chemical Society. 2016;14(3):655-63.