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ORIGINAL PAPER

Nanosilica molybdic acid: synthesis, characterization and application as a green and reusable catalyst for the Pechmann condensation

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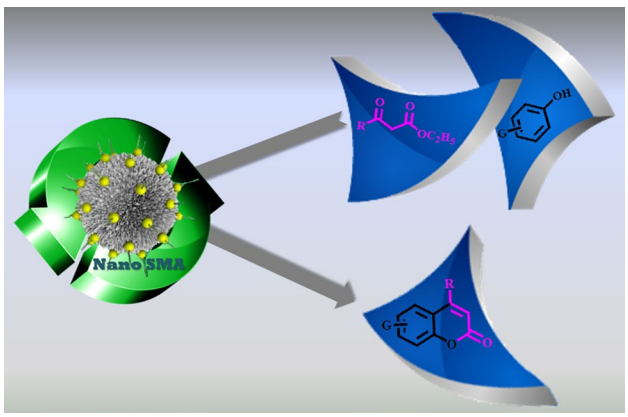
Abstract Nanosilica molybdic acid (SMA NPs) was founded as an efficient and recyclable nanocatalyst for the synthesis of coumarin derivatives in excellent yields with good purity. Nano-SMA as a new solid acid was characterized by X-ray fluorescence, X-ray diffraction, energy-dispersive X-ray analyzer, transmission electron microscopy and Fourier transform infrared spectroscopy. Coumarin derivatives were obtained via the Pechmann condensation reaction of phenols and β-ketoesters at 80 °C under solvent-free conditions. The main advantages of the present procedure are high yields, shorter reaction time and green chemistry procedure, simple work-up and inexpensive and reusability of the catalyst.

Graphical Abstract



Keywords Nanosilica molybdic acid · Coumarins · Pechmann condensation · Solvent-free conditions · Nanocatalyst

Introduction

In recent years, one of the growing and important fields is nanotechnology. Because of different physical and chemical properties of nanosized catalysts compared to bulk material, they attract interest for different research areas [1]. Since the particles are in small size, the surface area exposed to the reactant is maximized so allowing more reactions to occur at the same time; hence, the process is speeded up [2].

Application of heterogeneous catalysts in organic transformations has an important role, because they have many advantages such as decreased reactor, facile handling, plant corrosion problems and more environmentally safe disposal [3–6].

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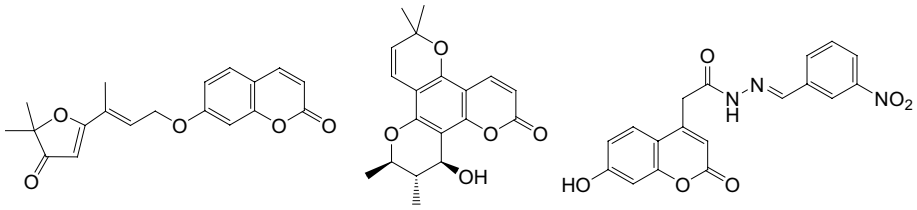


Fig. 1 Biologically active coumarin derivatives

Coumarin derivatives have attracted considerable interest because they exhibit a variety of biological activities such as antimicrobial, anti-inflammatory, analgesic, antioxidant, antimalarial, anticancer, antituberculosis and anti-HIV properties, which have been reviewed [7–15]. Some biologically active anticancer [16] and antituberculosis [17] agents having coumarin moiety are presented in Fig. 1.

Nowadays, many synthetic methods for preparing coumarins have been developed to improve and modify this reaction. However, in spite of their potential utility, many of these methods involve expensive reagents, strong acidic conditions, tedious work-up, low yields and long reaction times. Pechmann condensation under solvent-free conditions as an eco-friendly strategy since reduces waste production and precludes the use of organic solvents [18].

Several acid catalysts have been used in the Pechmann reaction, including nanocrystalline sulfated tin oxide [19], mesoporous zirconium phosphate (m-ZrP) [20], $BaCl_2$ [21], silica gel-supported zirconyl chloride octahydrate [22], $HClO_4SiO_2$ [23], alumina sulfuric acid [24], Zr-TMS-TFA-25 [25], poly (4-vinylpyridine)-supported copper iodide [26], PEG-SO_3H [27], zirconium (IV) phosphotungstate and 12-tungstophosphoric acid supported onto ZrO_2 [28].

In this work, a new methodology to obtain coumarins, via a one-pot Pechmann condensation, is reported. We introduce nanosilica molybdic acid (SMA NPs) as a novel and safe catalyst for the synthesis of coumarin derivatives.

Experimental

General

The chemicals were purchased from Merck and Aldrich chemical companies. The silica chloride **1** was synthesized according to the published procedure [29]. The reactions were monitored by TLC (silica gel 60 F 254, hexane: EtOAc). Fourier transform infrared (FT-IR) spectroscopy spectra were recorded on a Shimadzu-470 spectrometer, using KBr pellets, and the melting points were determined on a KRUSS model instrument. ^{1}H NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer at 400 MHz, in which DMSO-d_6 was used as solvent and TMS as the internal standard. X-ray diffraction (XRD) pattern was obtained by Philips X Pert Pro X diffractometer operated with a Ni-filtered Cu-Kα radiation source. X-ray fluorescence (XRF) spectroscopy was recorded by X-ray Fluorescence Analyzer, Bruker, S_4 Pioneer, Germany. EDAX analyses were carried out on a Philips XL30, operated at a 20-kV accelerating voltage. Transmission electron microscopy (TEM) images of the electrocatalyst were recorded using a Philips CM-10 TEM microscope operated at 100 kV.

General procedure for the preparation of nanosilica molybdic acid 2

To an oven-dried (125 °C, vacuum) sample of silica gel 60 (10 g) in a round-bottomed flask (250 ml) equipped with a condenser and a drying tube, thionyl chloride (40 ml) was added and the mixture in the presence of $CaCl_2$ as a drying agent was refluxed for 48 h. The resulting white-grayish powder was filtered and stored in a tightly capped bottle [29]. For 30 min, 0.1 g of silica chloride **1** was stirred in toluene (10 ml). The solution of 0.084 g sodium molybdate in 10 ml toluene was added to the first solution and stirred for 10 min. The resulting mixture was sonicated in an ultrasonic bath for 1 h at room temperature. The mixture was transferred to a 70-ml autoclave and heated at 140 °C for 4 h. White precipitate obtained, washed with distilled water, then separated by filtration and dried at 30 °C for 2 h. The white powder was stirred in HCl (0.1 N) for 1 h. The white powder was separated by filtration, washed with distilled water and dried at 30 °C for 2 h.

General procedure for the synthesis of coumarin derivatives 5a–o

In a general experimental procedure, β-ketoester **3** (1 mmol) was added to a mixture of substituted phenol **4** (1 mmol) and SMA NPs **2** (5 mol%) in a solvent-free tube. The reaction mixture was stirred in a preheated oil bath (80 °C). After the completion of the reaction, the precipitate obtained was extracted with ethyl acetate, washed with water (3 × 10 ml) and dried to obtain the product. The remaining insoluble solid catalyst in aqueous phase was separated by filtration, washed with ethyl acetate

(3 × 10 ml) and reused for further catalytic cycles. The crude product was recrystallized to afford the pure product.

Representative spectral data

*7-Hydroxy-4-methyl-2H-chromen-2-one (**5a**)*

Colorless prisms, mp 183–185 °C; yield 93%. ^{1}HNMR(400 MHz, DMSO-d_6): δ 10.138 (s, 1H), 7.373 (m, 5H), 6.722 (s, 1H), 6.470 (s, 1H), 5.957 (s, 1H), 2.292 (s, 3H).^{13}CNMR (100 MHz, DMSO-d_6):δ 160.09, 156.05, 155.96, 155.51, 143.93, 139.75, 128.34, 127.92, 127.75, 113.88, 112.52, 108.19, 105.44, 21.65. IR (KBr, cm^{-1}): (3000–3400), 3050, 2900, 1690, 1615, 1590, 1500, 1080.

*7-Hydroxy-4-phenyl-2H-chromen-2-one (**5b**)*

Colorless prisms, mp 246–248 °C; yield 86%. ^{1}HNMR (400 MHz, $CDCl_3$): δ 5.905 (s, 1H), 6.56 (m, 2H), 7.04 (d, 1H), 7.28 (t, 1H), 7.322 (m, 3H), 10.65 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 103.12, 110.10, 111.08, 113.68, 128.54, 128.79, 129.29, 130.07, 135.52, 155.9. IR (KBr, cm^{-1}): 3050, 1690, 1600, 1250, 1150.

*5-Hydroxy-4,7-dimethyl-2H-chromen-2-one (**5d**)*

Colorless prisms, mp 250–252 °C; yield 96%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 10.52 (s, 1H), 6.62 (d, 1H, J = 1.2 Hz), 6.57 (d,1H, J = 1.2 Hz), 6.03 (d, 1H, J = 1.2 Hz), 2.54 (d, 3H, J = 1.2 Hz), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.29, 156.90, 155.28, 154.04, 143.18, 112.37, 112.3, 108.15, 106.96, 23.91, 21.56. IR (KBr, cm^{-1}): 3393 (OH), 1655 (C=O).

*5-Hydroxy-7-methyl-4-phenyl-2H-chromen-2-one (**5e**)*

Colorless prisms, mp 214–216 °C; yield 88%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 10.14 (s, 1H), 7.35 (m, 5H,), 6.72 (s, 1H), 6.47 (s, 1H), 5.96 (s, 1H), 3.01 (s, 3H). ^{13}CNMR (100 MHz, DMSO-d_6): δ 160.09, 156.05, 155.96, 155.51, 143.93, 139.75, 128.34, 127.92, 127.75, 113.88, 112.52, 108.19, 105.44, 21.65. IR (KBr, cm^{-1}): 3180 (OH), 1680 (C=O).

*5,7-Dihydroxy-4-methyl-2H-chromen-2-one (**5g**)*

White solid, mp 279–281 °C; yield 91%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 10.51 (1H, s), 10.28 (1H, s), 6.24 (1H, s), 6.15 (1H, s), 5.83 (1H, s), 2.49 (3H, s). ^{13}CNMR(100 MHz, DMSO-d_6): δ 16.51, 160.55, 158.39, 156.96, 155.43, 109.22, 102.55, 99.45, 94.98, 23.88. IR (KBr cm^{-1}): 3400, 3070, 2940, 1670, 1600, 1480, 1080.

*7-Methoxy-4-methyl-2H-chromen-2-one (**5j**)*

Colorless prisms, mp 161–163 °C; yield 88%. ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.50 (d, 1H, J = 8.8 Hz), 6.87 (dd, 1H, J = 8.8, 2.4 Hz), 6.83 (d, 1H, J = 2.4 Hz), 6.14 (d, 1H, J = 1.2 Hz), 3.88 (s, 3H), 2.40 (d, 3H, J = 1.2 Hz). ^{13}CNMR (100 MHz, $CDCl_3$): δ 162.83, 160.59, 155.24, 153.86, 126.88, 113.56, 112.54, 111.58, 101.16, 56.36, 18.58. IR (KBr, cm^{-1}): 3400 (OH), 1705 (C=O).

*7,8-Dihydroxy-4-methyl-2H-chromen-2-one (**5n**)*

White solid, mp 235–237 °C; yield 75%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 10.1 (s, 1H), 9.35(s,1H), 7.07 (d, 1H, J = 8.8 Hz), 6.81 (d, 1H, J = 8.4 Hz), 6.12 (d, 1H, J = 1.2 Hz), 2.4 (d, 3H, J = 1.2 Hz). ^{13}CNMR (100 MHz, DMSO-d_6): δ 160.71, 154.35, 149.81, 143.47, 132.60, 115.88, 113.23, 112.56, 110.60, 18.63. IR (KBr, cm^{-1}): 3231 (OH), 1668 (C=O).

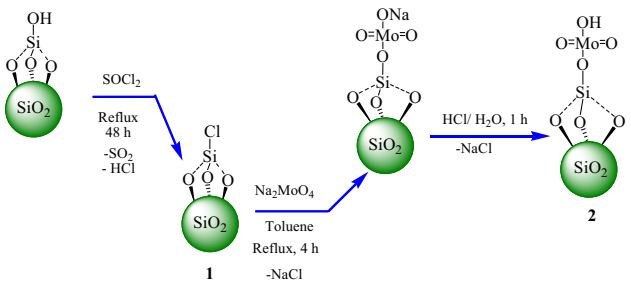
*7-Amino-4-methyl-2H-chromen-2-one (**5o**)*

Light yellow solid, mp 220–222 °C; yield 94%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 7.4 (d, 1H, J = 8.8 Hz), 6.56 (d, 1H, J = 7.2 Hz), 6.39 (s, 1H), 6.09 (s, 2H), 5.89 (s, 1H), 2.39 (s, 3H). ^{13}CNMR (100 MHz, DMSO-d_6): δ 160.90, 152.80, 151.00, 148.00, 127.60, 113.00, 112.50, 111.10, 106.70, 21.2. IR (KBr, cm^{-1}): 3439 (N–H), 1684 (C=O).

Results and discussion

Nanosilica molybdic acid was synthesized and characterized by X-ray fluorescence (XRF), X-ray diffraction pattern (XRD), Fourier transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDAX) and transmission electron microscopy (TEM).

In continuation of our previous studies on the development of various catalysts in the synthesis of organic compounds [30–32], as can be seen in Scheme 1, SMA NPs **2**



Scheme 1 Synthesis of nanosilica molybdic acid **2**

Table 1 XRF data of SMA NPs **2**

Entry	Compound	Concentration (%)
1	SiO_2	71.14
2	MoO_4	25.62
3	Na_2O	1.90
4	Cl	0.460
5	ZnO	0.355
6	CaO	0.289
7	Fe_2O_3	0.046
8	Al_2O_3	0.045
9	CuO	0.027
10	GeO_2	0.023
11	MnO	0.022
12	TiO_2	0.022
13	Total	99.95

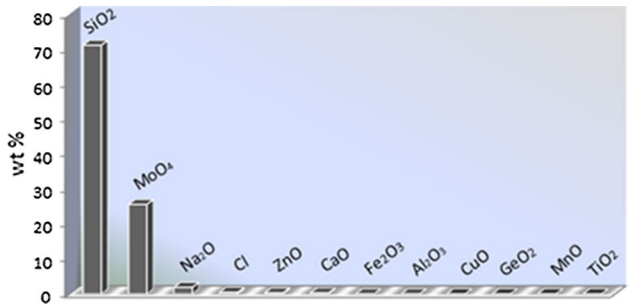


Fig. 2 XRF analysis of SMA NPs **2**

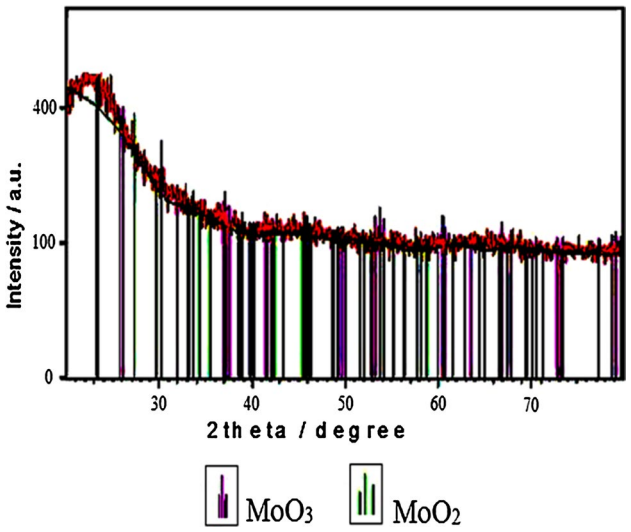


Fig. 3 XRD pattern for SMA NPs **2**

was prepared from the reaction of readily available materials such as silica gel, thionyl chloride and silica chloride **1** [33]. Accordingly, we found that anhydrous sodium molybdate can react with **1** to give nanosilica molybdic acid (SMA NPs) **2**. This reaction is clean and easy. From the synthetic point of view, the nucleophilic substitution of silicon is also attractive. The amount of H^+ was determined by back titration of the weighed amount of catalyst with standard 0.1 N NaOH solution that was found to be equal to 0.25 mmol/g of the catalyst.

As can be seen in Table 1, XRF data for the SMA NPs **2** show the composition of the catalyst as 71.14 (%W/W) SiO_2 and 25.62 (%W/W) MoO_4 (Fig. 2).

Figure 3 shows the XRD patterns for the SMA NPs **2** which exhibits the presence of molybdic acid crystalline phase supported on amorphous silica as a broad peak around 23° (2θ) (θ is Bragg's angle). The three peaks in the 35°–40° region of the XRD spectrum could be attributed to the presence and linking of MoO_3 to the silica gel [34].

The FT-IR spectra for the anhydrous sodium molybdate, silica chloride and SMA NPs **2** are shown in Fig. 4. This spectrum shows the characteristic bonds of anhydrous sodium molybdate and silica chloride.

The successful incorporation of molybdate groups was also confirmed by EDAX analysis (Fig. 5), which showed the presence of Mo in addition to Si and O elements.

The adsorption in 3452, 1634, 1086, 800 cm^{-1} in the catalyst spectrum reveals both bonds in SiO_2–Cl and MoO_4 group. We evaluated that the amount of H^+ was determined by back titration of the weighed amount of catalyst with standard 0.01 N NaOH solution and was found to be equal to 0.25 mmol of the catalyst.

The structural information about nanosilica molybdic acid such as particle size and shape was provided by transmission electron microscopy (TEM). As shown in Fig. 6, the TEM image revealed the formation of mesostructured nanoparticles with an average size in the range of 15–30 nm.

To study the efficiency of SMA NPs **2** for Pechmann condensation, the reaction of β-ketoesters **3** and phenol derivatives **4** was selected as the model. The expected coumarins **5a–o** were obtained as pure products in high yield by solvent-free stirring (Scheme 2).

This reaction was firstly examined in the absence of catalyst which did not show any appreciable progress even after 360 min. Silica gel and silica chloride as catalysts could not show promising catalytic effects. When the reaction was tried with Na_2MoO_4 and sodium silica molybdate as catalysts, the product was obtained in low yield in longer time period. However, when the reaction was tried using SMA NPs as a catalyst, the results obtained were very satisfactory as good yield of the product (93%) was obtained at 20 min only (Table 2, entry 1). Upon screening, the results well showed that the reaction proceeds efficiently

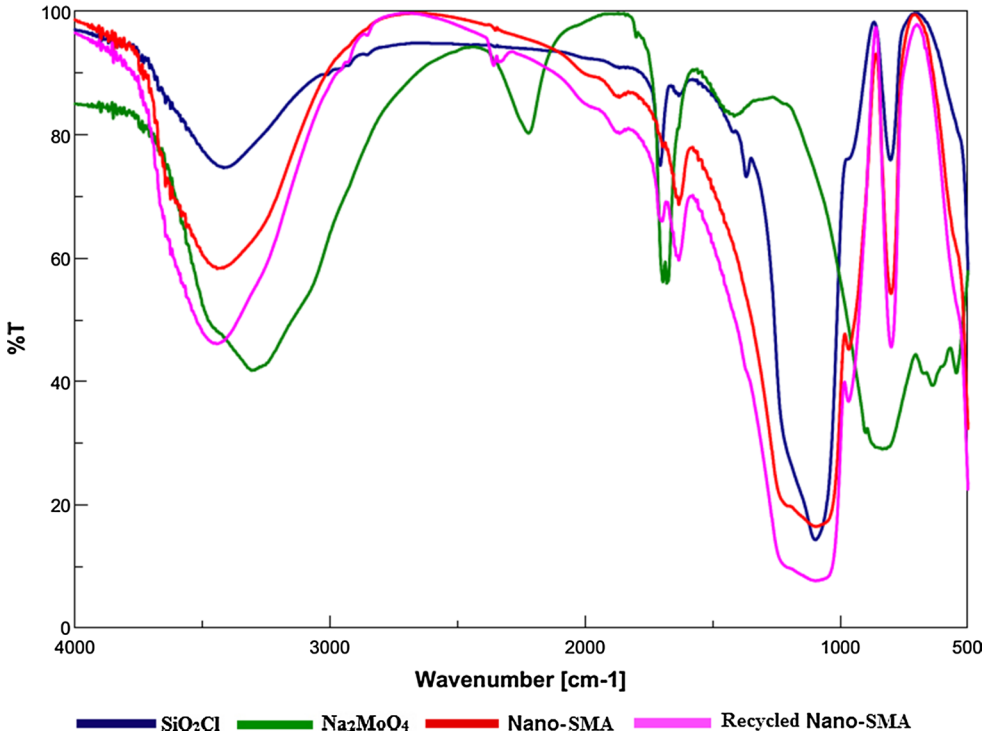


Fig. 4 FT-IR spectra for the comparison of SiO_2Cl, Na_2MoO_4, SMA NPs 2 and recycled SMA NPs **2**

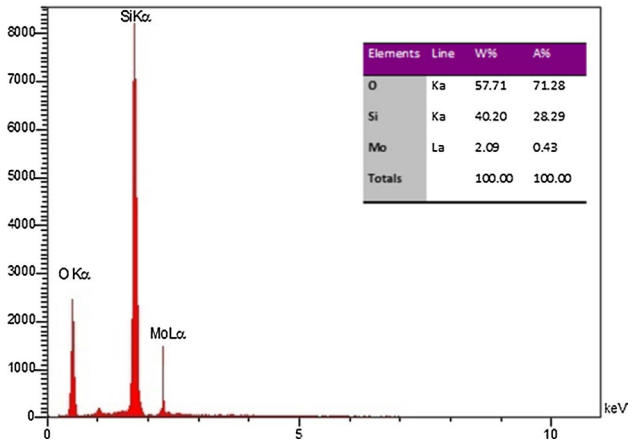


Fig. 5 Energy-dispersive spectroscopy (EDAX) pattern of SMA NPs **2**

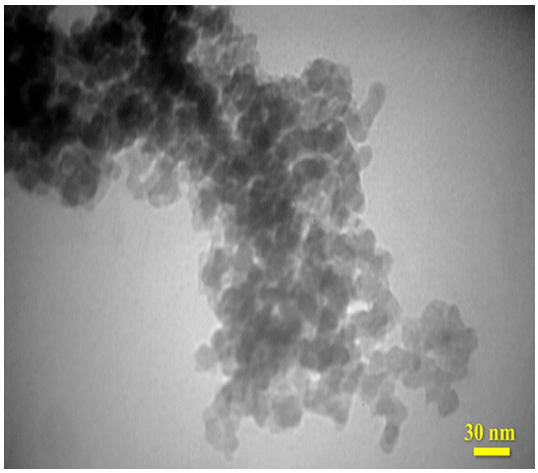


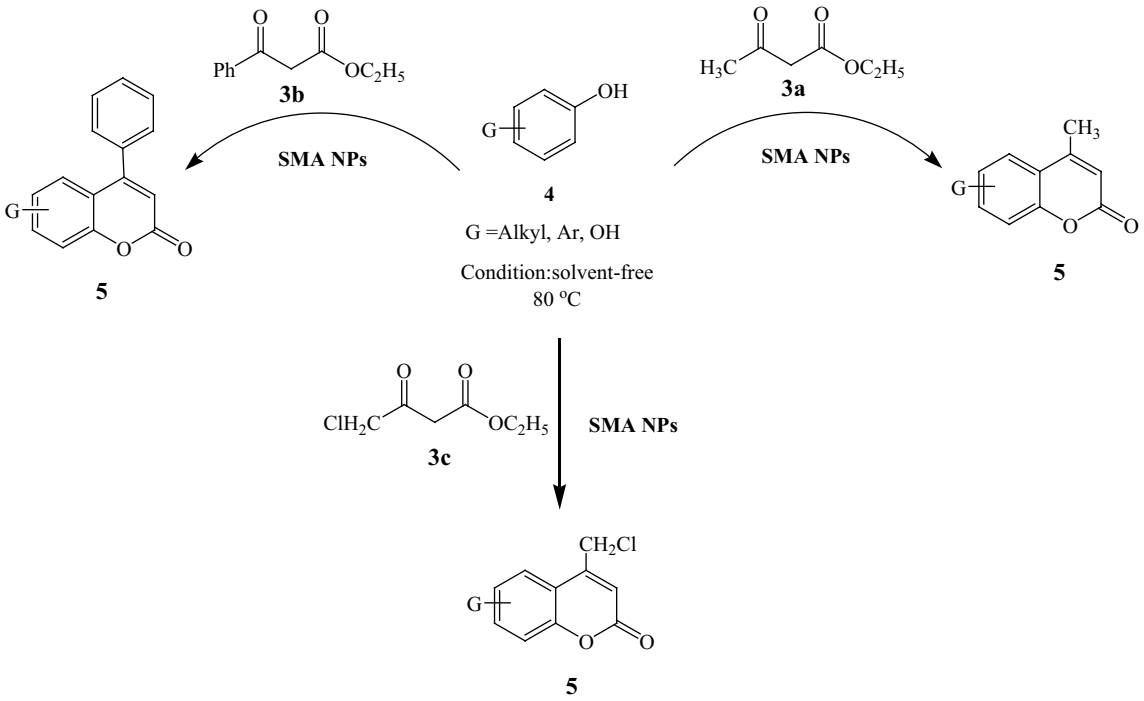
Fig. 6 TEM image of SMA NPs **2**

by adding 5 mol% of SMA NPs. Also, increasing the catalyst amount did not improve the results (Fig. 7).

After optimization of the reaction conditions, as can be seen in Fig. 7, in order to extend the scope of this reaction, various phenols such as resorcinol, pyrogallol and phloroglucinol were successfully used for the efficient Pechmann reaction with different β-ketoesters. A wide variety of coumarins were obtained through this method in good-to-excellent yield in short reaction times.

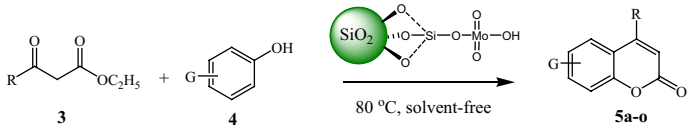
Coumarin **5a** was synthesized in 93% yield for 20 min (monitored by TLC CCl_4–ethyl acetate 5:1). Coumarin **5a** was characterized by IR, NMR and other spectral data. Similarly, resorcinol was treated with ethyl 4-chloroacetoacetate, ethyl benzoylacetate (Table 2, entries 2, 3) to furnish coumarins (**5b**, **5c**), respectively.

Encouraged by the above results, other phenolic substrates were subjected to the Pechmann reaction using SMA NPs. In all cases, the reactions proceeded successfully to afford the corresponding coumarins in good-to-excellent yields. The electron-donating substituents in the meta-position to the phenolic –OH facilitated the cyclization. The reactivity of phloroglucinol (1,3,5-trihydroxybenzene)



Scheme 2 SMA NPs-catalyzed synthesis of coumarins

Table 2 Synthesis of coumarins via von Pechmann condensation of phenols with β-ketoesters catalyzed by SMA NPs



Entry	R	G	Product	Time (min)	Mp. (°C) [lit.]	Yield[a] (%)
1	Me	3-OH	**5a**	20	183–185 [31]	93
2	Ph	3-OH	**5b**	90	246–248 [31]	86
3	CH_2Cl	3-OH	**5c**	15	176–178 [31]	84
4	Me	3-Me-5-OH	**5d**	25	250–252 [31]	96
5	Ph	3-Me-5-OH	**5e**	50	214–216 [31]	88
6	CH_2Cl	3-Me-5-OH	**5f**	15	163–165 [31]	87
7	Me	3,5-$(OH)_2$	**5g**	15	279–281 [31]	91
8	Ph	3,5-$(OH)_2$	**5h**	20	243–245 [31]	76
9	CH_2Cl	3,5-$(OH)_2$	**5i**	20	184–186 [31]	84
10	Me	3-MeO	**5j**	25	161–163 [31]	88
11	CH_2Cl	3-MeO	**5k**	20	177–179 [31]	85
12	Me	1-Naphthol	**5l**	30	154–156 [31]	78
13	CH_2Cl	1-Naphthol	**5m**	100	166–168 [31]	67
14	Me	2,3-$(OH)_2$	**5n**	40	235–237 [31]	75
15	Me	3-NH_2	**5o**	20	220–222 [31]	94

[a] Yields refer to isolated products

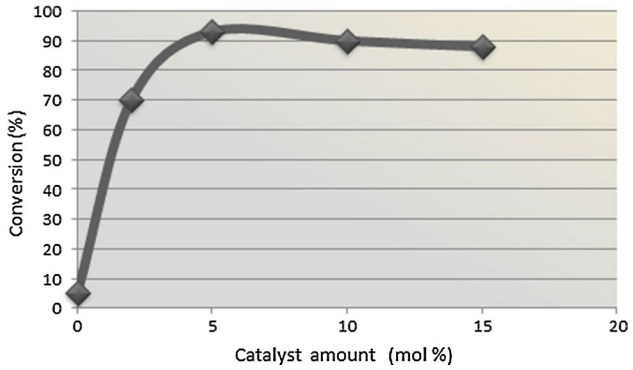


Fig. 7 Optimization of the catalyst amount

(entry 7) with ethyl acetoacetate was observed to be higher than pyrogallol (entry 14) due to two hydroxyl groups at meta-positions in phloroglucinol compared to one hydroxy group in pyrogallol. Presence of the *meta*-hydroxy group strongly activates the substrates due to resonance effect. *m*-Methoxyphenol (entry 10) showed no detectable demethylation under the reaction conditions. Similarly, 1-naphthol (entry 12) requires a slightly higher temperature and longer reaction time. These results show that the reactivity of phenolic substrates as the catalyst acidity is important. Finally, the reactions are remarkably clean, and no chromatographic separation is necessary to get the spectra-pure compounds.

The suggested mechanism for the Pechmann condensation of phenols **4** with β-ketoesters **3** in the presence of SMA NPs catalyst (Scheme 3) has been described using condensation as probe reaction. The SMA NPs catalyst would cause dehydration and produce an olefinic bond; at the same time, ethyl alcohol would be eliminated with the formation of coumarin ring.

Comparing this method with other catalysts, the synthesis of 7-hydroxy-4-methyl-2H-chromen-2-one (Table 2, Entry 1) as a model reaction was performed in the presence of other catalysts [31]. The results are shown in Table 3. The data show that our method is suitable and better than the others to synthesize coumarins with respect to the amounts of the used catalysts, reaction times and yields of the products (Table 3).

The design and synthesis of recoverable catalysts is a highly challenging interdisciplinary field, which combines chemistry, materials science and engineering from economic and environmental perspectives. The main disadvantage for many of the reported methods is that the catalysts are destroyed in the work-up procedure and cannot be recovered or reused. In this process,

Scheme 3 The proposed mechanism for the SMA NPs-catalyzed formation of coumarins

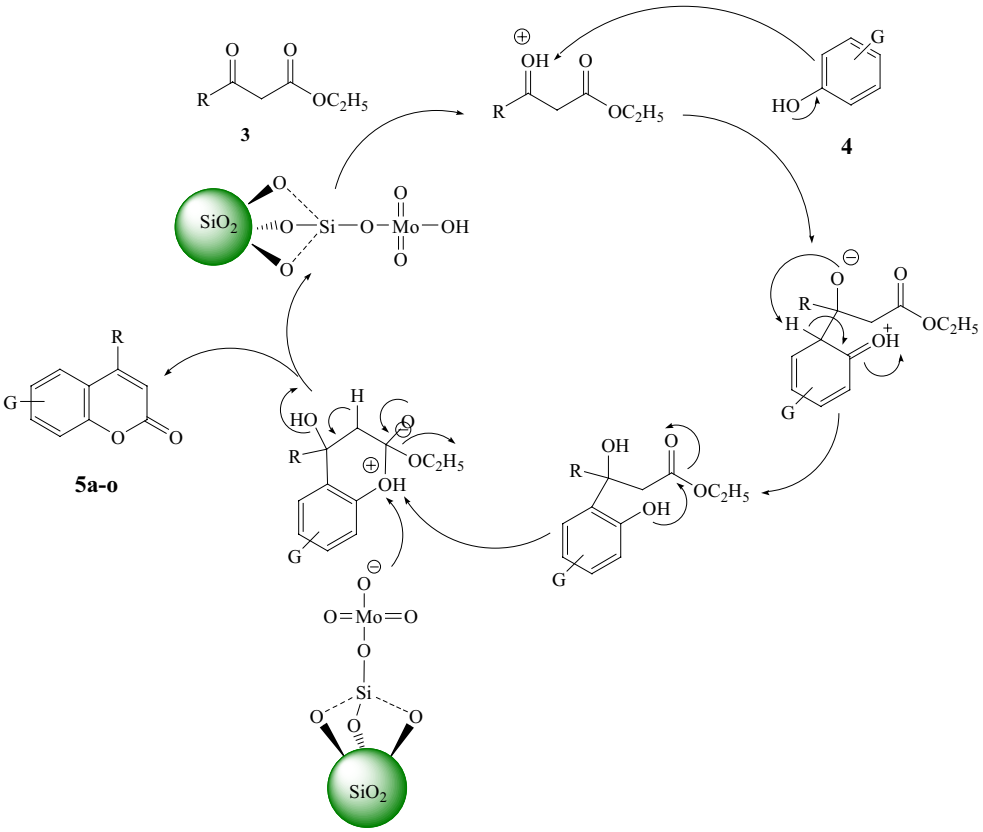


Table 3 Comparison of our method with other methods for the synthesis of (**5a**)

Catalyst	Catalyst amount	Condition	Time (min)	Yield (%)
SMA NPs	5 mol%	Solvent-free, 80 °C	20	93
ZrPW	0.2 g	Solvent-free, 130 °C	480	58
Nanocrystalline sulfated tin oxide	25 wt%	Solvent-free, 120 °C	240	95
Zr-TMS-TFA-25	0.1 g	Solvent-free, 100 °C	540	88
Mesoporous zirconium phosphate (m-ZrP)	15 wt%	Solvent-free, 160 °C	240	94
$ZrOCl_2{\cdot}8H_2O/SiO_2$	10 mol%	Solvent-free, 80 °C	10	98
$In(OTf)_3$	1 mol%	Solvent-free, 80 °C	32	87
$Y(NO3)_3{\cdot}6H_2O$	10 mol%	Solvent-free, 90 °C	45	92
$H_3PW_{12}O_{40}$ supported on nanoparticle tin oxide	30 wt%	Solvent-free, 120 °C	120	78

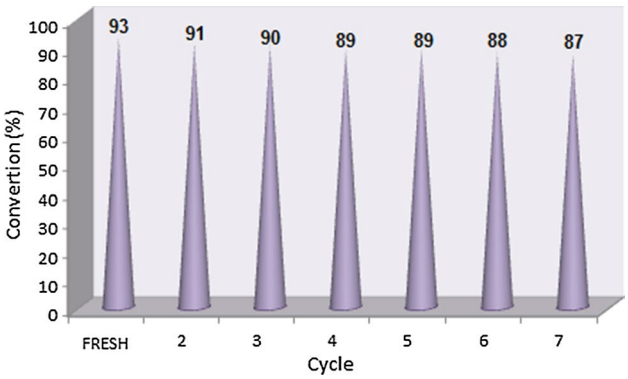


Fig. 8 Recyclability of SMA NPs as a catalyst for the synthesis of **5a**

as outlined in Fig. 8, the recycled catalyst can be used for up to six cycles, during which there are negligible losses in the catalytic activity. The FT-IR spectra of the catalyst after six cycles (Fig. 4) showed the same spectral fingerprint of the freshly prepared catalyst indicating the stability of the catalyst throughout the recycling experiment.

Conclusions

In summary, we found SMA NPs as an effective and environmentally safe heterogeneous catalyst which successfully catalyzed the Pechmann condensation reaction to produce coumarins of potential synthetic and pharmaceutical interest was presented. The present protocol not only originates the products with excellent yields in short reaction times but also avoids some problems such as catalyst cost, pollution, handling and safety. Also, conventional work-up of products and high recyclability of catalyst are other attractive features of this procedure.

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References

1. B. Morak-Miodawska, K. Pluta, Heterocycles **78**, 1289 (2009)
2. M. Moreno-Manas, R. Pleixats, Acc. Chem. Res. **36**, 638 (2003)
3. K. Niknam, M.A. Zolfigol, T. Sadabadi, A. Nejati, J. Iran. Chem. Soc. **3**, 318 (2006)
4. B. Karimi, D. Zareyee, Org. Lett. **10**, 3989 (2008)
5. J.A. Melero, R.V. Grieken, G. Morales, Chem. Rev. **106**, 3790 (2006)
6. B. Karimi, M. Khalkhali, J. Mol. Catal. A Chem. **232**, 113 (2005)
7. M.E. Riveiro, N.D. Kimpe, A. Moglioni, R. Vazquez, F. Monczor, C. Shayo, C. Davio, Curr. Med. Chem. **17**, 1325 (2010)
8. L. Wu, X. Wang, W. Xu, F. Farzaneh, R. Xu, Curr. Med. Chem. **16**, 4236 (2006)
9. F. Borges, F. Roleira, N. Milhazes, L. Santana, E. Uriarte, Curr. Med. Chem. **12**, 887 (2005)
10. X.M. Peng, G.L.V. Damu, C.H. Zhou, Curr. Pharm. Des. **19**, 3884 (2013)
11. A. Lacy, R. O'Kennedy, Curr. Pharm. Des. **10**, 3797 (2004)
12. I. Kostova, Med. Chem. **5**, 29 (2005)
13. M.A. Musa, J.S. Cooperwood, M.O.F. Khan, Curr. Med. Chem. **15**, 2664 (2008)
14. M.V. Kulkarni, G.M. Kulkarni, C.H. Lin, C.M. Sun, Curr. Med. Chem. **13**, 2795 (2006)
15. C. Kontogiorgis, A. Detsi, D.H. Litina, Expert Opin. Ther. Pat. **22**, 437 (2012)
16. K.V. Sashidhara, S.R. Avula, K. Sharma, G.R. Palnati, S.R. Bathula, Eur. J. Med. Chem. **60**, 120 (2013)
17. R.J. Naik, M.V. Kulkarni, K.S.R. Pai, P.G. Nayak, Chem. Biol. Drug Des. **80**, 516 (2012)
18. M.A.P. Martins, C.P. Frizzo, D.N. Moreira, L. Buriol, P. Machado, Chem. Rev. **109**, 4140 (2009)
19. S. Ghodke, U. Chudasama, Appl. Catal. A **453**, 219 (2013)
20. B.M. Reddy, M. Patil, P. Lakshmanan, J. Mol. Catal. A Chem. **256**, 290 (2006)
21. S. Khodabakhshi, Org. Chem. Int. **2012**, 1 (2012)
22. B. Karami, M. Kiani, Catal. Commun. **14**, 62 (2011)
23. M. Maheswara, V. Siddaiah, G. Lakishmi, V. Damu, Y.K. Rao, C.V. Rao, J. Mol. Catal. A Chem. **255**, 49 (2006)
24. A. Amoozadeh, M. Ahmadzadeh, E. Kolvari, J. Chem. **2013**, 1 (2013)
25. K. Jung, Y.J. Park, J.S. Ryu, Synth. Commun. **38**, 4395 (2008)
26. J. Albadi, F. Shirini, J. Abasi, N. Armand, T. Motaharizadeh, C. R. Chim. **16**, 407 (2013)
27. G.M. Nazeruddin, M.S. Pandharpatte, K.B. Mulani, C. R. Chim. **15**, 91 (2012)
28. S. Ghodke, U. Chudasama, Appl. Catal. A Gen. **453**, 219 (2013)

29. A. Cornelis, P. Laszlo, Synthesis **10**, 909 (1985)
30. B. Karami, M. Kiani, M.A. Hoseini, Chin. J. Catal. **35**, 1206 (2014)
31. B. Karami, M. Kiani, J. Chin. Chem. Soc. **61**, 213 (2014)
32. M. Kiani, B. Karami, J. Chin. Chem. Soc. **62**, 756 (2015)
33. H. Karade, M. Sathe, M.P. Kaushik, Catal. Commun. **8**, 741 (2007)
34. T. Brezesinski, J. Wang, S.H. Tolbert, B. Dunn, Nat. Mater. **9**, 146 (2010)