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Ultrasonic-assisted preparation of nano eggshell powder: A novel catalyst in green and high efficient synthesis of 2-aminochromenes

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Abstract

The nano eggshell powder (NESP) has been prepared by ultrasound irradiation and used as a novel and biodegradable catalyst with high catalytic activity and reusability in green synthesis of 2-aminochromenes via condensation of α- or β-phathol, malononitrile and aromatic aldehydes at 125 °C under solvent-free conditions. The reaction proceeds to completion within 10-35 min in 91-98% yield. Nano eggshell catalyst was characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and X-ray fluorescence, thermal gravimetric, surface area and elemental analyses. In addition, the catalytic activity and chemical structure of nano-sized eggshell were compared with pure $CaCO_3$.

Keywords: Nano eggshell powder, Sonochemical preparation, natural catalyst, XRD, 2-aminochromenes, green chemistry

1. Introduction

Eggs are consumed worldwide because they contain all essential amino acids, vitamins, and minerals. Eggshell waste primarily contains calcium, magnesium carbonate (lime) and protein [1] and is the significant solid waste produced from food processing and manufacturing plants [2]. This natural solid waste, although non-hazardous, is commonly disposed in landfills without any pretreatment because it was traditionally useless [3]. As a consequence, a huge problem of pollution is generated. In addition, it can attract rats and worms due the organic protein matrix, resulting in a problem of public health [4]. However, special attention has been devoted to industrial sectors that are sources of pollution of the environment [5, 6]. A topical area of great importance related to the waste processing and recycling approach is the proper characterization of the material [6]. In recent years, a great deal of effort has been conducted for the application of eggshell as value-added products. These major applications included a possible bone substitute [7], the starting material for preparing calcium phosphate bioceramics (e.g. hydroxyapatite) [8], coating pigments for inkjet printing paper [9], a low-cost adsorbent for removal of ionic pollutant and dyes from the aqueous solution [10,11] and lactose isomerisation [12]. Also, calcined eggshell (CaO) was used for biodiesel fuel production [13] and dimethyl carbonate [2] synthesis. Currently, there is a trend toward simple, low temperature and green method for the preparation of nanoparticle. One of the novel, powerful and simple method for the synthesis of nanomaterial is sonochemistry [14,15] that led to high activity in catalysis due to their particles size and high surface area [16]. Also, the ultrasonic irradiation provides a clean media to prepare nanomaterials in short reaction time. The chemical and physical effects of ultrasonic irradiation originate from acoustic cavitations [17, 18].

2-Aminohromenes are widely employed as pigments, cosmetics, potential biodegradable agrochemicals and also as components of many natural products [19-21]. Also, They show antidepressant, antihypertensive, anti-tubulin, antiviral and antioxidative activity [22,23]. The most straightforward synthesis of this heterocyclic system involves a three-component coupling of aromatic aldehyde, malononitrile and activated phenol in the presence of organic bases like piperidine in an organic solvent such as ethanol or acetonitrile for several hours [24]. Although a number of modifications of this reaction conditions have been reported [25-40], but, all these methods include some or other drawbacks such as low yields, prolonged reaction time, tedious catalyst preparation and workup, and exhaustive usage of energy sources and solvents. So, the development of an efficient and green methodology for the synthesis of 2-aminochromenes is highly essential.

Heterogeneous base catalyzed organic synthesis is a promising field of research with potential application in pharmaceuticals and related fine chemical industries [41–46]. Recently, we found that waste eggshell could be used as an active heterogeneous and micro-porous catalyst for 4*H*-benzo[*b*]pyrans synthesis [47]. It was proved that eggshell was an interesting unconventional heterogeneous biocatalyst for organic synthesis. Since eggshell has a little porosity, we decided to explore ultrasonic assisted preparation of nanopowder catalyst based on eggshell waste and investigate its catalytic properties as a solid base mesoporous catalyst for 2-aminochromenes synthesis via one pot multi-component condensation of aryl aldehydes, malononitrile and α or β-naphthol in solvent-free and thermal conditions. The other aim was to compare the catalytic activity of pure $CaCO_3$ and nano-sized mesoporous eggshell catalysts.

2. Experimental

2.1. Materials and Instruments

All chemicals were of analytical grade, purchased from Merck and used as received. Ultrasonic irradiation was performed in an ultrasound cleaning bath (FALC instrument, Italy) with a frequency of 60 Hz and voltage of 220 V. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded at 500 (^{1}H) and 125.77 (^{13}C) MHz on Bruker DRX-500 Avance spectrometer at 500 and 125.77 MHz, respectively. IR spectra were obtained with MATSON 1000 FT-IR spectrophotometer.

X-ray diffraction (XRD) with a D8 Bruker diffractometer (40kV and 40mA) and Cu $_{K\alpha}$ radiation (λ=0.154 nm) was used to analyze the crystal structure of the milled powders. The XRD patterns were recorded in the 2θ range of 20-80º with the step size of 0.01º. The mean size and size distribution of the eggshell powder were measured by a dynamic laser light scattering (DLS) apparatus (FRITSCH Analysette 22 NanoTec Laser Particle Sizer). The chemical composition of the catalyst was determined using a X-ray fluorescence (XRF) Microanalyser (Unisantis XMF-104, Germany) with 40kV, 300mA and Mo radiation. TGA experiments were carried out using a STA 409 PC Luxx thermal analysis machine (NETZSCH, Germany) under a flow of nitrogen. The sample weight used was about 20 mg, and the temperature ranged from 25 to 900 °C with a ramping rate of 10 °C/min. The morphology of the cross section of the film was examined with a field emission scanning electron microscope (FESEM) after being fractured in liquid nitrogen. Dried samples were coated with gold ions using an ion coater at 150 s. Surface structure was visualized by field emission scanning electron microscope (Hitachi S4160) using a 15 kV accelerating voltage. TEM images were obtained on a LEO912-AB (LEO, Germany) transmission electron microscope with an accelerating voltage of 120 kV. Particles were deposited onto a carbon foil supported by a copper grid. The Milling was carried out in a planetary ball mill using hardened chromium steel vial (250 ml) at room temperature under argon atmosphere. It was performed using hardened chromium steel vial (250 ml). The ball-to-powder weight ratio and the rotation speed of the vial were 350 rpm and 10:1 respectively.

2.2. Catalyst preparation

Empty chicken eggshells were collected from the household and washed with tap warm water. The adhering membrane was separated manually. Then, the eggshells were washed with distilled water and dried at 120°C for 1 h. Then the eggshells were milled in a planetary ball mill for 2 h. Next, the eggshell powder was mixed with CH_2Cl_2 and placed in an ultrasonic cleaning bath with a frequency of 60 Hz at 50°C for 1 h. Since eggshell is a hydrophobic compound, an organic and aprotic solvent is needed to dissolve and remove the rest of the organic materials from the eggshell. These impurities often remain in the eggshell even after washing and drying in oven. It is likely that the presence of these impurities in the eggshell, affect the average surface area and catalytic activity of the eggshell catalyst. So, a purification process such as that described above may remove these impurities. Also, it was observed that a small amount of solvent (CH_2Cl_2, 5 mL) was necessary to stabilize the suspension of eggshell nanocrystals to avoid high agglomeration. After ultrasonication, the powder was filtered from the solvent and dried at room temperature. The eggshell particle size was obtained with laser particle sizer.

2.3. General procedure for the preparation of 2-aminochromene-2-carbonitriles

In a typical general procedure, a mixture of 3-nitrobenzaldehyde (0.15 g, 1 mmol), malononitrile (0.07 g, 1 mmol) and α or β-naphthol (0.14 g, 1 mmol) in solvent-free condition at 125 °C, were stirred thoroughly in the presence of a catalytic amount of NESP (0.1 g) to afford the corresponding 2-aminochromene in excellent yields. After completion of the reaction (TLC), hot EtOH was added to the reaction mixture and stirred for 5 min. Then the solid catalyst was filtered from the soluble products and washed with hot EtOH. After cooling, the crude products were precipitated. Pure 2-aminochromenes were obtained in high yields without any use of more purification. All compounds were known in the literature [25-40] and the NMR and IR spectra of the products were in agreement with earlier data [25-40]. The selected spectral data of two representative 2-aminochromene derivatives are given

3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (Table 3, entry 7). IR (KBr): 3455, 3336, 2196, 1669, 1600, 1571, 1415, 1377, 1100 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ = 8.15 4.86 (s, 2H, NH_2); 5.32 (s, 1H, CH), 7.41–7.20 (m, 5H), 7.45–7.51 (m, 1H), 7.86–7.89 (m, 2H), (d, J = 9.7 Hz, 2H),

2-Amino-4-(4-chlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (Table 3, entry 2). IR (KBr): 3454, 3336, 2192, 1669, 1601, 1575, 1414, 1378, 1100, 878 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ = 4.78 (br s, 2H, NH_2), 4.85 (s, 1H, CH), 7.01 (d, J= 8.7 Hz, 1H, Ar), 7.19-7.47 (m, 5H, Ar), 7.50-7.58 (m, 2H, Ar), 7.78 (d, J=7.1 Hz, 1H, Ar); 8.15 (d, J= 8.2 Hz, 1H);

3. Results and Discussion

3.1. Characterization of nanocatalyst

3.1.1. Chemical composition of nano eggshell powder

XRF and Elemental analysis of mesoporous eggshell showed high levels of Ca (35.2%) and carbon (13%), P (0.75%), O (48.01%), with small amounts of Mg (1.61%), Sr (0.6%), Si (0.3%), K (0.075%), Na (0.054%), Fe (0.03%), Zn (0.03%), Ni (0.01%), Cl (0.028%), nitrogen (0.30%), and hydrogen (0.05%).

3.1.2. Particle size and BET surface area analysis

The higher S_{BET} with smaller size of catalyst particles could provide higher reaction conversion [48]. Table 1 presents the particle size and the nitrogen physisorption data of natural eggshell and pure $CaCO_3$. The surface area of just ballmill treatment eggshell was 0.0253 $m^2\ g^{-1}$ with the average particle size of 35 µm, whiles they are 3.5421 $m^2\ g^{-1}$ and 3 µm for NESP (Table 1, entry 1,2) that proved a decrease in crystal size of the powder due to ultrasonic irradiation. As shown in Table 1, the low surface area with larger particle size of pure $CaCO_3$ and its sonicated ones (entries 3-6) processed low porosity. Since, the catalytic activity of the catalysts agreed well with the specific surface area and catalyst particle size, it is logical that mesoporous sonicated eggshell with downsized crystal can catalyze the reaction more effective than ballmilled eggshell powder and $CaCO_3$. Also, there was interested that we tried to prepare NESP using microwave irradiation, but our attempt was not successful.

Table 1.

3.1.3. Thermo Gravimetric Analysis (TGA)

Nanocatalyst was further analyzed by thermal gravimetric analysis in order to explain the effect of high temperature on its thermal stability (Fig. 1). DSC thermal curves representing the carbonate mineral are characterized by exothermic peaks with $\Delta H_f° = 1194$ J/g caused by the evolution of carbon dioxide. TGA result showed the temperatures, at which the eggshell precursors decomposed when heated in a controlled environment at a given ramp rate. The weight loss below 1.3 % at 600°C was related to release of physisorbed H_2O from the sample. Complete calcination was observed between 600-847°C with the weight loss of 46.2%, resulting in phase-change due to decomposition of $CaCO_3$ to CO_2 and CaO. So, the catalyst remained stable in the reaction temperature (125 °C) and CaO phase was found when the eggshell was calcined at 900 °C for 1 h.

Fig. 1.

3.1.4. XRD and FTIR analysis

Also, the prepared catalyst was characterized by infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The same XRD pattern of the nano eggshell powder and the commercially available $CaCO_3$ with $2\Theta = 29.4$ angles, indicating that calcite ($CaCO_3$) is a major phase of the waste eggshell (Fig. 2), and the NESP and the commercially available $CaCO_3$ have a very similar chemical nature. High XRD peak intensities of commercially available $CaCO_3$ than those of the eggshell catalyst are related to its larger $CaCO_3$ particle size [49]. The XRD patterns of pure $CaCO_3$ are the same as its ultrasonic treatment one . The major peak of calcite phase (2ϴ = 29.4) was not shown in XRD pattern of the calcined eggshell, implying that the $CaCO_3$ phase was completely transformed to CaO phase (Fig. 2c).

Fig 2.

Fig 3.

Fig. 3 shows the same strong characteristic carbonate bands of the nanocatalyst and the sonicated $CaCO_3$ in IR spectra. IR spectra of pure $CaCO_3$ and its ultrasonic treatment are exactly the same. The broad transmission band at approximately 3410 cm^{-1} can be attributed to OH stretching vibration from residual water [47]. The weak band at 1798 cm^{-1} corresponds to CO bonds from carbonate [50]. Two well-defined infrared bands at 1422 and 710 cm^{-1} are characteristic of the C–O stretching and bending modes of calcium carbonate, respectively [51]. The strong band at 876 $cm^{-1}$is related to OCO out of plane of vibration mode [47]. A medium broad band in 2517 cm^{-1} shows the presence of HCO_3. This data confirms the presence of $CaCO_3$ in the egg shell powder [51] and compare with published data of 1455-1470/1420-1425 cm^{-1} (ν_3), 1065-1075 cm^{-1} (ν_1), 863-873 cm^{-1} (ν_2) for $CaCO_3$ [52–55]. Fig **3c** shows the existence of peak at 3640 cm^{-1} is due to OH in $Ca(OH)_2$ formed during adsorption of water by CaO. So, the FTIR spectrum of eggshell powder indicates this product is hygroscopic and clearly has moisture water [56].

3.1.5. Electron microscope images

Transmission electron microscope (TEM) and Field Emission Scanning Electron Microscope (FESEM) are another useful tool for the analysis of the surface morphology of a catalyst. SEM images of just ballmilled treatment eggshell, sonicated calcium carbonate and NESP were given in fig 4. A comparative SEM images study was shown an increase in porosity of NESP and obviously illustrate the mesoporous nature of the catalyst with many distributed pores and pits over the entire eggshell surface. In general, the high porosity of the nano eggshell powder provides a large contact area for catalyzing the reaction (Fig. 4a ,b). The average size of the nanocrystals obtained from the TEM and FESEM images analysis is 50 nm.

Fig. 4.

3.2. General synthesis of 2-aminochromene derivatives

The activity of the green nanocatalyst was tested using a one-pot three-component condensation of α or β-naphthol (1 mmol) with different aromatic aldehydes (1 mmol) and malononitrile (1.5 mmol) under solvent-free and thermal conditions to obtain the corresponding 2-aminochromenes. Without the addition of a catalyst, the reaction produced only alkene **5** and no 2-aminochromenes **4** was formed even after 10 h in the reaction conditions (Fig. 5).

Fig. 5.

To develop optimum conditions, first, the effect of temperature and solvent on the rate of the reaction was studied for the preparation of 2-aminochromenes (Table 2). At 125 °C, the reactions proceeded to completion very rapidly. A decrease in temperature leads to decreasing product yields and rate of the reaction. It was observed that the reaction did not proceed at room temperature. In order to show the effect of ultrasonic irradiation on the catalytic activity of the NESP, next, a comparative reaction was carried out by using just ballmill treatment eggshell. As shown in Table 2 (entry 8), the reaction proceeds to completion in 75 min with product yield of 84%, while they are 35 min and 91% for its ultrasonic treatment one. This proves the essential effect of ultrasonic irradiation on the catalytic activity of eggshell powder as a mild and efficient catalyst in the reaction.

Table 2.

Next, the optimum amount of nanocatalyst was evaluated in the range of 0.02-0.2 g. The highest yield was obtained with 0.1 g of the catalyst. A further increase in the amount of catalyst up to 0.2 g did not have any significant effect on the product yield or reaction time. The generality of this reaction was examined using different aldehydes (Table 3). In all cases, the reactions gave the corresponding products in good to excellent yields (91-98%) and in very short reaction times (10-35 min). This method offers significant improvements with regard to the scope of the transformation, simplicity, and green aspects by avoiding expensive, hazardous or corrosive catalysts.

Table 3.

Among several heterogeneous basic catalysts, the alkali and alkaline earth metals are most promising [42,57]. Calcium carbonate is an interesting basic carbonate which shows well defined surface basicity and catalytic activity [32]. Since almost 90% of the eggshell is composed calcium carbonate and it is the main active site of eggshell catalyst, we carried out a comparative reaction in the presence of $CaCO_3$ (0.1 g) in the same conditions. It was interested that different byproducts with trace amounts of the desired product can be obtained after 24 h. In addition, the catalytic reactions by using $CaCO_3$ powder prepared under ultrasonic irradiation from 1 to 3 h were carried out and compared with the subject reaction using NESP. As shown in Table 2 (entry 10-12), the catalytic activity of $CaCO_3$ was increased with irradiation time because of downsize the powder due to ultrasonication.

However, compared with NESP catalyst, the reaction time was very long and the product yield was low. The eggshell product has an average porosity naturally and ultrasonic irradiation causes an increase in its porosity. It is probably because of the vapor of the solvent from the catalyst pores in high pressure and temperature that makes it more porous catalyst. As seen in BET and SEM analysis, NESP is very porous and its calcium carbonates have much higher surface area. Also, eggshell contains small amount of different ions (Mg, Sr, P, Si, K, Na, Fe, Ni and Cl) which can catalyze the reaction. But, as is clear, these small amounts of chemicals have low catalytic activity. However, a comparative reaction was carried out using sonicated $MgCO_3$ which has the highest amount after $CaCO_3$ (Table 2, entry 13). The result was shown the low catalytic activity of sonicated $MgCO_3$. This proved the highest catalytic activity of the NESP due to increase in porosity and decrease in crystal size of the catalyst because of ultrasonic irradiations.

3.3. Catalyst Recovery and Reusability

The reusability of catalysts is one of the most important benefits and makes them useful for commercial and industrial applications. The reusability of the catalyst was examined in the synthesis of 2-aminochromene-2-carbonitrile **4b** (Table 3, entry 7). The catalyst was recovered after each run, washed three times with hot EtOH, dried in an oven at 120 °C, and tested for its activity in subsequent runs.

Fig. 6.

It was found that the catalyst could be reused six times without any loss of activity. Thus, the new procedure is eco-friendly, cost effective, clean and more efficient than reported methods.

4. Conclusion

In summary, easily and rapidly sonochemical preparation of nano eggshell powder in a CH_2Cl_2 solution and its comparison with sonicated $CaCO_3$ structure has been explored. Also, a green, rapid and highly efficient protocol for the one-pot synthesis of 2-amino-4*H*-chromens has been described under thermal solvent-free conditions using eggshell waste as a heterogeneous nanocatalyst with high catalytic activity and reusability. This eggshell is a novel nanocatalyst base on eggshell waste which can catalyze the organic transformation and reduce environmental problems and it is the first use of this waste material as the nano-sized catalyst in organic synthesis.

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Figure Caption:

Scheme 1. Synthesis of 2-aminochromene derivatives catalyzed by nano eggshell powder (NESP)

Fig. 1. TGA curves of nano eggshell powder (NESP)

Fig. 2. XRD pattern of (a) black line: commercially available $CaCO_3$; (b) red line: NESP; (c) blue line: calcined eggshell

Fig. 3. FTIR spectra of NESP (a), sonicated $CaCO_3$ (b) and calcined eggshell (c).

Fig. 4. TEM and SEM images of NESP (a); ballmill treatment eggshell powder (b); sonicated calcium carbonate for 3 h (c).

Fig. 5. Benzilidene malononitrile intermediate

Fig. 6. Recycling experiment of NESP

Table 1. BET surface area (S_{BET}), and average particle size of eggshell powder and pure $CaCO_3$.

Entry	Sample	Surface area[a] (m^2g^{-1})	Average particle size[b] (µm)
1	eggshell	3.5421	3
2	ballmilled eggshell	0.3265	35
3	$CaCO_3$	0.0145	49
4	$CaCO_3$,[c] US 1 h	0.0215	47
5	$CaCO_3$,[c] US 2 h	0.0823	44
6	$CaCO_3$,[c] US 3 h	0.1061	41

[a] Determined by N_2 adsorption analysis.

[b] Determined by laser particle sizer.

[c] Pure $CaCO_3$ were irradiated in ultrasonic for appropriate time according to experimental section.

Table 2. Effect of solvent, temperature and type of catalyst in the reaction condensation of 3-nitrobenzaldehyde, α-naphthol and malononitrile.

Entry	Conditions	Catalyst	Time	Yield (%)[a]
1	H_2O, r.t	NESP (0.1 g)	24 h	—
2	H_2O, 45°C	NESP (0.1 g)	24 h	trace
3	EtOH, r.t	NESP (0.1 g)	24 h	trace
4	EtOH, 45°C	NESP l (0.1 g)	10 h	trace
5	solvent-free, 125 °C	—	10 h	—
6	solvent-free, 80 °C	NESP l (0.1 g)	95 min	85
7	solvent-free, 125 °C	NESP (0.1 g)	35 min	91
8	solvent-free, 125 °C	ballmilled eggshell (0.1 g)	75 min	84
9	solvent-free, 125 °C	$CaCO_3$ (0.1g)	24 h	trace
10	solvent-free, 125 °C	$CaCO_3$ (0.1g),[b] US 1 h	19 h	69
11	solvent-free, 125 °C	$CaCO_3$ (0.1g),[b] US 2 h	16 h	77
12	solvent-free, 125 °C	$CaCO_3$ (0.1g),[b] US 3 h	14 h	80
13	solvent-free, 125 °C	$MgCO_3$ (0.005g),[b] US 3 h	24 h	trace

[a] Yields refer to the isolated products.

[b] Pure $CaCO_3$ and $MgCO_3$ were irradiated in ultrasonic bath for appropriate time.

Table 3. Synthesis of 2-aminochromene derivatives catalyzed by NESP under thermal and solvent-free conditions.

Entry	Product	R	Time (min)	Yield[a] (%)
1	4a	$3\text{-}NO_2\text{-}C_6H_4$	20	94
2	4a	$4\text{-}Cl\text{-}\ C_6H_4$	25	93
3	4a	$3\text{-}Br\text{-}\ C_6H_4$	30	98
4	4a	$2\text{-}CH_3O\text{-}\ C_6H_4$	10	97
5	4a	$2,4\text{-}Cl_2\text{-}\ C_6H_3$	20	96
6	4a	$4\text{-}OH\text{-}\ C_6H_4$	15	93
7	4b	$3\text{-}NO_2\text{-}C_6H_4$	35	91
8	4b	$4\text{-}Cl\text{-}\ C_6H_4$	20	92
9	4b	$3\text{-}Br\text{-}\ C_6H_4$	25	97
10	4b	$2\text{-}CH_3O\text{-}\ C_6H_4$	10	95
11	4b	$2,4\text{-}Cl_2\text{-}\ C_6H_3$	15	95
12	4b	$4\text{-}OH\text{-}\ C_6H_4$	15	94

[a] Yield refers to isolated pure product.

Figure

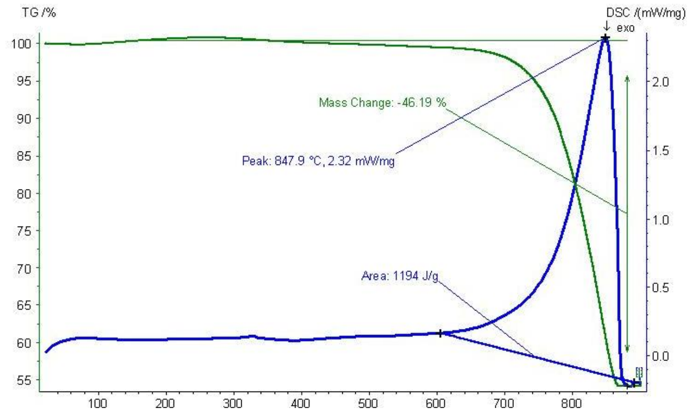

Fig. 1. TGA curves of nano eggshell powder (NESP).

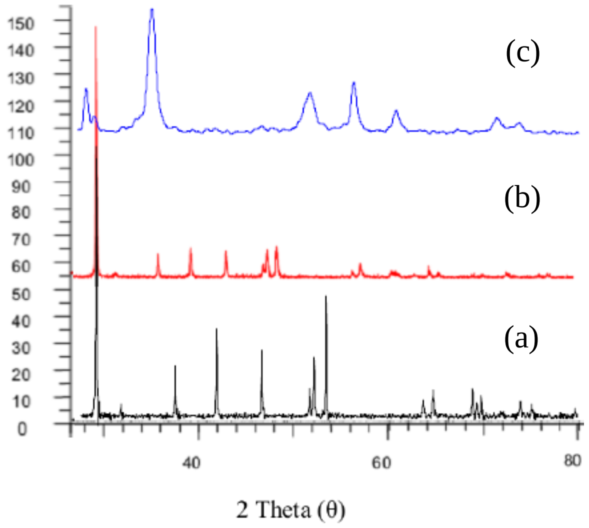

Fig. 2. XRD pattern of (a) black line: commercially available $CaCO_3$; (b) red line: NESP; (c) blue line: calcined eggshell.

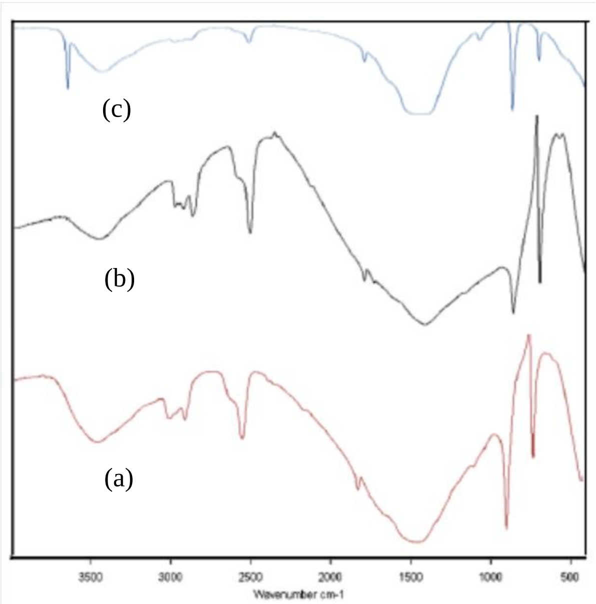

Fig. 3. FTIR spectra of NESP (a), sonicated $CaCO_3$ (b) and calcined eggshell (c).

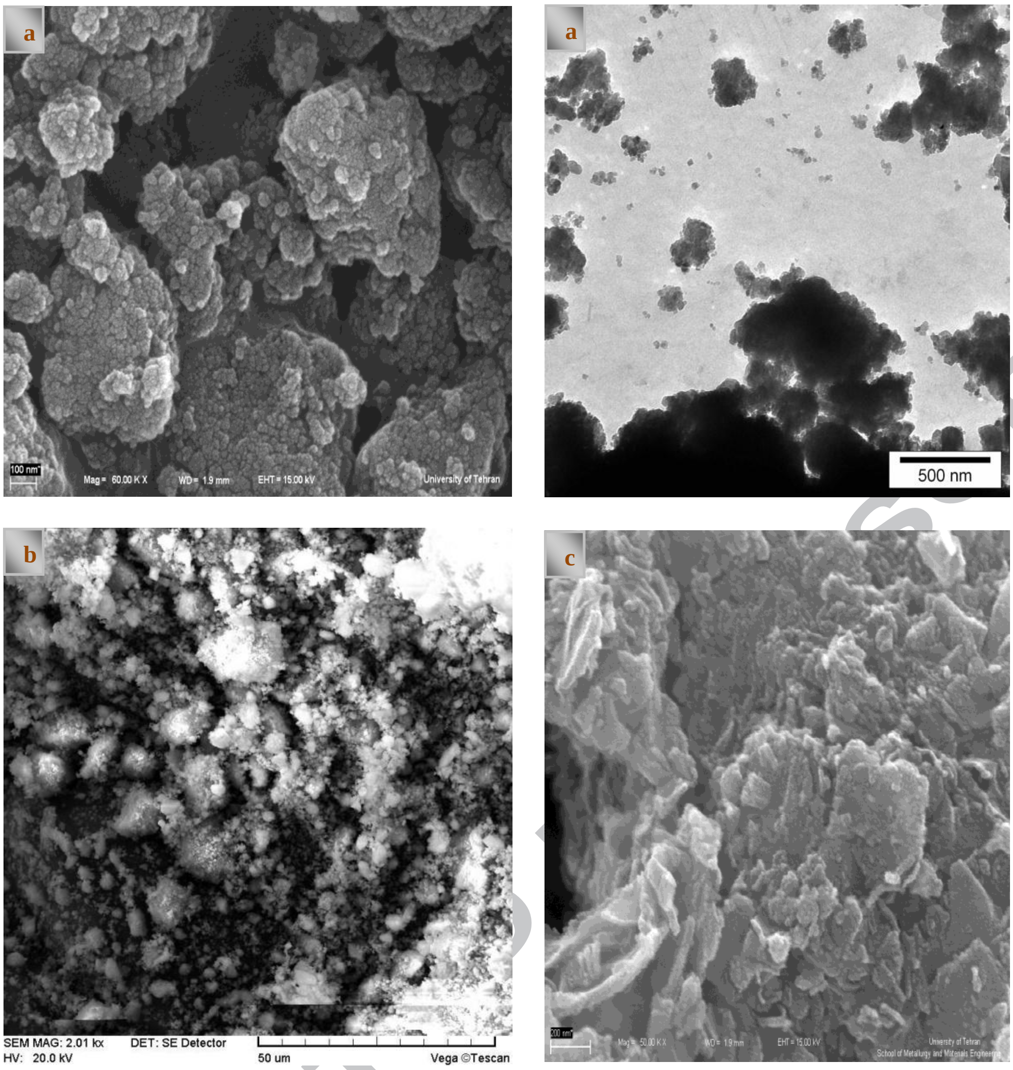

Fig. 4. TEM and SEM images of NESP (a); ballmill treatment eggshell powder (b); sonicated calcium carbonate for 3 h (c).

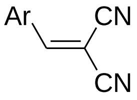

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Fig. 5. Benzilidene malononitrile intermediate

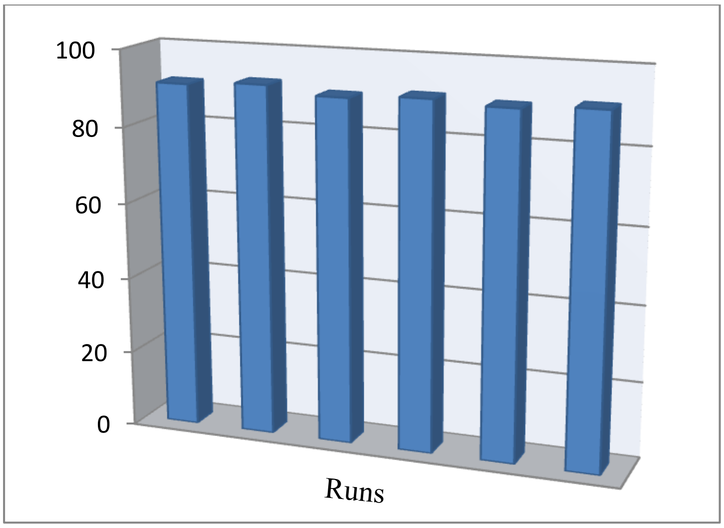
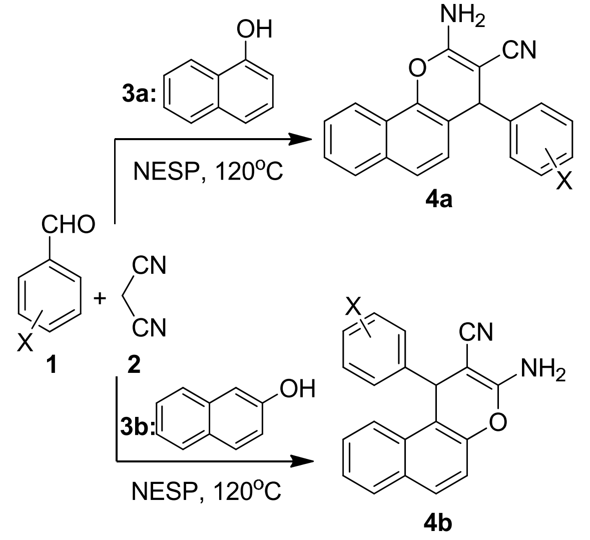


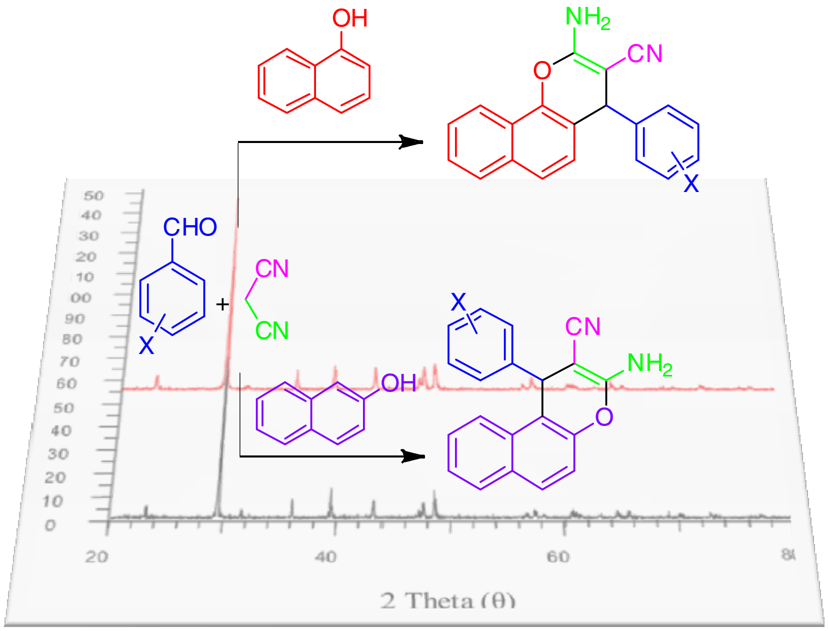
Fig. 6. Recycling experiment of NESP

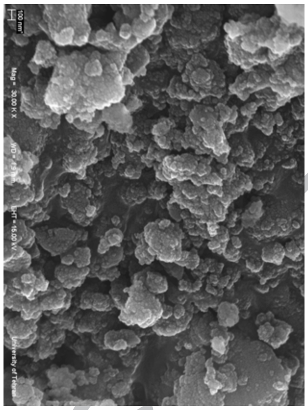


Scheme 1. Synthesis of 2-aminochromene derivatives catalyzed by nano eggshell powder (NESP)

Highlights:

- Ultrasonic-assisted preparation of nano eggshell powder (NESP) has been developed
- Eggshell Characterization with XRD, XRF, IR spectra, BET, TGA, TEM and FESEM.
- Green and rapid synthesis of 2-aminochromenes in the presence of nanosized eggshell
- High catalytic activity and reusability of nano catalyst even after five cycles
- Catalytic activity comparison of pure $CaCO_3$ and NESP as heterogeneous catalyst





Nano eggshell powder

Graphical Abstract