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# Strongly proton exchanged montmorillonite K10 (H<sup>+</sup>-Mont) as a solid acid catalyst for highly efficient and environmental benign synthesis of biscoumarins via tandem Knoevenagel-Michael reaction

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**Abstract:** In this study, synthesis of micro/meso porous acid-activated montmorillonite K10 (H<sup>+</sup>-Mont) was carried out by the activation of Na<sup>+</sup>-montmorillonite with HCl (4 M) at the controlled conditions. The prepared H<sup>+</sup>-Mont clay was then characterized using FT-IR, SEM, EDX, XRD and BET analyses. SEM and BET surface analyses represented that by the acid-activation, adjacent layers of montmorillonite K10 (Mont K10) were exfoliated to tiny segments leading to raise of surface area and total pore volume in H<sup>+</sup>-Mont system rather than the alone Mont K10. Catalytic activity of the prepared H<sup>+</sup>-Mont clay was further studied as a potent solid acid catalyst for synthesis of biscoumarin materials via tandem Knoevenagel-Michael reaction of 4-hydroxycoumarin with aromatic aldehydes. All reactions were carried out in a mixture of H<sub>2</sub>O-EtOH (1:1) at room temperature to afford the products in high to excellent yields within 25–50 min.

Keywords: Knoevenagel-Michael; Biscoumarin; H⁺-Mont; 4-Hydroxycoumarin; Montmorillonite K10

### 1. Introduction

Catalysts owing to their indisputable role in gaining goals of green chemistry have always been a subject of more interest. Highly atom economy reactions, minimizing hazardous chemicals and eliminating the need for harsh reaction conditions are some of the precious benefits which are only accessible by designing and selecting the proper catalysts in chemical processes [1]. In this area, applying solid heterogeneous catalysts which are inexpensive, non-toxic, easily separable and recoverable from the reaction mixture is a key approach [2–5]. In recent years a variety of heterogeneous catalytic systems such as zeolite based catalysts [6–9], magnetically recyclable nanocatalysts [10, 11], natural biopolymers [12–15] and clays [16–19] have been successfully used in organic synthesis.

Clays are abundant, readily available and eco-friendly mineral solids that made up from layered silicates. Clay minerals commonly occur in two basic building blocks including tetrahedral and octahedral sheets. As well, depending to the degree of octahedral sites occupancy, they are also consisted from dioctahedral or trioctahedral sheets [16–19]. Montmorillonite K10 (Mont K10) has a dioctahedral layer structure. Clay minerals generally has a molecular formula of  $M_x(Al_{2-x}Mg_x)(Si_4)O_{10}(OH)_2 \cdot nH_2O$  [20] in which M is exchangeable ion in the interlayers. Cation-exchange ability in interlayer of montmorillonite makes it a tunable acid catalyst. Based on this idea, some Brønsted and Lewis acidic catalysts could be prepared by replacing H<sup>+</sup>, Ti<sup>4+</sup>, Cu<sup>+2</sup> and various other transition metals in the interlayers [21–24]. Although, montmorillonite K10 inherently has acidic properties, however, replacing the cations of interlayers with proton increases its Brønsted acidity, specific surface area and catalytic activity even more [16–19]. Montmorillonite K10, because of its eco-friendly nature, low cost, cation-exchange and swelling abilities has become one of the most intensively focused catalytic materials in the realm of clays and heterogeneous catalysts [20]. So, it has been frequently used for catalysis of several transformations [25–29].

Coumarins are one of outstanding family of natural products occurring in various plant species [30–32]. In this context, biscoumarins are also well known and have been found some pharmaceutical properties including anticoagulant [33], antibacterial [34], antifungal [34] and anti-inflammatory [35]. In addition, some new biscoumarin derivatives exhibited antitumor [36], anti HIV [37], urease inhibitor [38], anti-microbial [39], radical scavengers and chain-breaking antioxidant activities [40].

In line with the outlined strategies, herein, we wish to report the synthesis of proton exchanged montmorillonite K10 (H<sup>+</sup>-Mont) as a potent solid acid catalyst for highly efficient and environmental benign

synthesis of biscoumarin materials via tandem Knoevenagel-Michael reaction of aromatic aldehydes with 4-hydroxycoumarin in a mixture of  $EtOH-H_2O$  (1:1) at room temperature (Figure 1).



Figure 1. Synthesis of biscoumarins 3(a-I) catalyzed by H<sup>+</sup>-Mont clay

### 2. Experimental

### 2.1. Materials and methods

All chemicals were purchased from chemical companies with the best quality and they were used without further purification. <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR spectra were recorded on 300 MHz Bruker Avance and Thermo Nicolet Nexus 670 spectrometers. X-ray diffraction (XRD) measurements were carried out on a X'PertPro Panalytical, Holland diffractometer in 40 kV and 30 mA with a CuK $\alpha$  radiation ( $\lambda$ =1.5418 Å). Signal data were recorded in 2 $\theta$  = 10°–80° with a step interval of 0.05°. Morphology and size distribution of nanoparticles were examined by scanning electron microscopy (SEM) using FESEM-TESCAN MIRA3 instrument. The chemical composition of the prepared nanostructured clays was determined by energy-dispersive X-ray (EDX) spectroscopy. The specific surface area and total pore volume of the samples were measured by Brunauer-Emmett-Teller technique on Belsorp-Max instrument (Japan). The pore size distributions were derived by using Barrett-Joyner-Halenda method. Melting points were recorded on Electrothermal 9100 melting point apparatus and uncorrected. Yields refer to isolated pure products. TLC was applied for monitoring of the reactions over silica gel 60 F254 aluminum sheet. Montmorillonite K10 was purchased from Sigma-Aldrich company with art No. 69866 (pH ~ 3–4, surface area: 250 m<sup>2</sup>/g). All products are known and were characterized by comparison of their physical and spectral data with those of authentic samples.

### 2.2. Preparation of homoionic Na<sup>+</sup>-exchanged montmorillonite (Na<sup>+</sup>-Mont)

In a beaker (250 mL) containing distilled water (200 mL), montmorillonite K10 (5 g) was added and the mixture was stirred vigorously at room temperature for 20 h. The mixture was then allowed to settle and the aqueous phase was decanted. To the obtained solid residue, an aqueous solution of NaCl (2 M, 200 mL) was added and the mixture was continued to stirring for 2 h at room temperature. The aqueous phase was decanted and the solid residue was again charged with an aqueous solution of NaCl (2 M, 200 mL). After stirring for 2 h at room temperature, the aqueous phase was decanted. The procedure was repeated for additional two times. Finally, the solid residue was washed frequently with distilled water until the conductivity of the liquid filtrate reaches to the conductivity of distilled water. The solid residue was dried at 50 °C under air atmosphere to afford homoionic Na<sup>+</sup>-exchanged montmorillonite (Na<sup>+</sup>-Mont) [41].

### 2.3. Preparation of acid-activated montmorillonite [H<sup>+</sup>-Mont]

To a round-bottom flask (250 mL) containing an aqueous solution of HCl (4M, 100 mL), Na<sup>+</sup>-Mont (5 g) was added. The mixture was stirred under reflux conditions for 2 h. After cooling, the aqueous phase was decanted and the residue was washed frequently with distilled water. When the liquid filtrate was free of

 $Cl^-$  (testing with AgNO<sub>3</sub>), the solid material on filter paper was collected and dried at 50 °C to afford acidactivated montmorillonite (H<sup>+</sup>-Mont) [41].

### 2.4. A general procedure for synthesis of biscoumarins using H<sup>+</sup>-Mont clay

In a round-bottom flask (15 mL) containing a mixture of  $H_2O$ -EtOH (1:1 mL), 4-hydroxycoumarin (2 mmol), aromatic aldehyde (1 mmol) and H<sup>+</sup>-Mont (0.02 g) were added. The mixture was stirred magnetically at room temperature for an appropriate time mentioned in Table 4. After completion of reaction (monitored by TLC), the clay catalyst was removed from the reaction mixture. The filtrate was evaporated and the solid material was recrystallized from hot ethanol to obtain the pure biscoumarins **3(a-I)** (Table 4, 85-95% yields).

### 2.5. Determining cation-exchange capacity (CEC) of a clay mineral

Measuring cation-exchange capacity (CEC) of a clay mineral was carried according to the reported procedure [41]. To do this, a clay mineral (such as Mont K10) (0.5 g) was dispersed in a standard alcoholic solution of  $CaCl_2$  (10 mL, 0.05 M) and the prepared mixture was stirred at room temperature for 24 h. The suspension was filtered, washed with EtOH (20 mL) and dried at room temperature for 12 h. The  $Ca^{2+}$ -exchanged clay mineral was then transferred to a volumetric flask (250 mL). By adding distilled water, the volume of flask was reached to standard limit (250 mL). The amount of  $Ca^{2+}$  was titrated with a standard solution of EDTA. The difference in  $Ca^{2+}$ concentration, before and after cation-exchange, affords CEC (meq·g<sup>-1</sup>) amount of a clay mineral.

Spectra data for the prepared biscoumarin materials:

### 3,3'-(Phenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3a)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3400, 3067, 2737, 1659, 1609, 1564, 1336, 1089, 755; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.11 (s, 1H, CH), 7.25-8.07 (m, 13H, ArH), 11.32 (s, 1H, OH), 11.55 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 36.16, 103.88, 105.62, 116.42, 116.65, 124.39, 124.91, 126.89, 128.77, 132.88, 135.17, 152.27, 164.60, 165.02.

### 3,3'-(4-Chlorophenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3b)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3428, 3073, 2730, 1664, 1614, 1565, 1494, 1344, 1094, 770; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.04 (s, 1H, CH), 7.15-8.06 (m, 12H, ArH), 11.32 (s, 1H, OH), 11.55 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.7, 103.69, 105.24, 116.34, 124.41, 125.01, 127.97, 128.77, 132.77, 133.04, 133.83, 152.26, 164.53, 166.02.

### 3,3'-(2-Chlorophenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3c)

FT-IR (KBr, υ cm<sup>-1</sup>): 3069, 2720, 1649, 1556, 1498, 1444, 1340, 1097, 760; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 6.16 (s, 1H, CH), 7.27-8.04 (m, 12H, ArH), 10.93 (s, 1H, OH), 11.64 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 35.72, 116.59, 124.42, 124.87, 126.76, 128.59, 129.24, 130.81, 132.83, 133.49, 162.33.

### 3,3'-(2,4-Dichlorophenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3d)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3068, 2719, 2594, 1649, 1565, 1497, 1097, 759; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.12 (s, 1H, CH), 7.24-8.02 (m, 11H, ArH), 11.67 (s, 2H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.46, 116.51, 124.48, 124.87, 126.9, 130.33, 132.92, 134.1, 152.01, 164.22, 166.8.

### 3,3'-(4-Bromophenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3e)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3428, 3068, 2930, 1663, 1612, 1563, 1490, 1445, 1342, 1315, 1200, 1096, 1022, 767; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.02 (s, 1H, CH), 7.09-8.06 (m, 12H, ArH), 11.32 (s, 1H, OH), 11.54 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.86, 103.64, 105.18, 116.36, 116.66, 120.87, 124.4, 124.97, 128.3, 131.69, 134.4, 152.28, 162.34, 164.63, 166.02.

### 3,3'-(4-Methoxybenzylidene)-bis(4-hydroxy-2H-chromen-2-one) (3f)

FT-IR (KBr, υ cm<sup>-1</sup>): 3064, 2944, 2842, 2727, 1666, 1612, 1562, 1507, 1447, 1343, 1309, 1094, 768; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 3.80 (s, 3H, OMe), 6.05 (s, 1H, CH), 6.84-8.05 (m, 12H, ArH), 11.34 (s, 1H, OH), 11.52 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 33.37, 110.93, 116.5, 116.7, 120.4, 123.5, 124.3, 124.7, 128.2, 128.4, 132.44, 152.13, 157.56, 163.7, 165.2.

### 3,3'-(2-Methoxyphenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3g)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3412, 3069, 2981, 2724, 1654, 1620, 1550, 1494, 1448, 1337, 1305, 1094, 758; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.5 (s, 3H, OMe), 6.09 (s, 1H, CH), 6.85-8.04 (m, 12H, ArH), 11.22 (bs, 2H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.48, 104.18, 105.74, 113.98, 116.62, 116.89, 124.36, 124.86, 126.90, 127.61, 132.83, 152.25, 152.47, 164.51, 165.69, 169.25.

### 3,3'-(p-Tolylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3h)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3100, 2992, 2919, 1665, 1614, 1563, 1502, 1440, 1094, 765; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 2.34 (s, 3H, CH<sub>3</sub>), 6.07 (s, 1H, CH), 7.12-8.04 (m, 12H, ArH), 11.34 (s, 1H, OH), 11.48 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 20.97, 35.87, 116.61, 116.93, 124.37, 124.84, 126.36, 129.33, 132.77, 136.46, 152.47, 162.34, 164.5, 165.67.

### 3,3'-(4-Hydroxyphenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3i)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3361, 3072, 2731, 1660, 1614, 1565, 1509, 1443, 1096, 762; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.02 (s, 1H, CH), 6.77-8.02 (m, 12H, ArH), 11.48 (bs, 2H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 35.49, 104.16, 115.64, 116.61, 124.37, 126.78, 127.75, 152.41, 154.66, 162.32.

### 3,3'-(4-Nitrophenylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3j)

FT-IR (KBr, υ cm<sup>-1</sup>): 3427, 3075, 2935, 1652, 1562, 1343, 1095, 762; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 6.14 (s, 1H, CH), 7.27-8.17 (m, 12H, ArH), 11.39 (s, 1H, OH), 11.58 (s, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 36.18, 103.22, 104.62, 116.26, 116.73, 121.76, 122.12, 124.5, 125.17, 129.59, 132.7, 133.33, 137.9, 148.75, 152.35, 162.34, 166.59, 166.9.

### 3,3'-(2-Nitrophenyl)methylene)-bis(4-hydroxy-2H-chromen-2-one) (3k)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3433, 3076, 2722, 1652, 1618, 1561, 1532, 1450, 1352, 1309, 1099, 761; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 6.64 (s, 1H, CH), 7.27-8.01 (m, 12H, ArH), 11.55 (bs, 2H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 33.86, 103.71, 116.66, 124.57, 125.03, 128.19, 129.49, 131.9, 133.2, 149.76.

### 3,3'-(4-Pyridylmethylene)-bis(4-hydroxy-2H-chromen-2-one) (3I)

FT-IR (KBr,  $\upsilon$  cm<sup>-1</sup>): 3447, 3075, 2880, 1663, 1618, 1543, 1500, 1407, 1102, 757; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) 6.47 (s, 1H, CH), 7.21-8.68 (m, 12H, ArH and pyridy-H). It is notable that, due deuterium exchange, hydrogen of two OH groups at region of  $\delta$  = 11.5 ppm was not observed. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) 38.26, 101.88, 116.20, 119.82, 123.65, 124.67, 125.67, 132.04, 141.35, 153.15, 164.53, 165.34, 168.59.

### 3. Results and discussion

### 3.1 Synthesis and characterizations of micro/meso porous acid-activated montmorillonite K10 (H<sup>+</sup>-Mont)

The study was primarily started by the preparation of H<sup>+</sup>-Mont clay nanocatalyst in a three-step procedure (Figure 2): i) preparation of swelled (hydrated) montmorillonite via vigorous stirring of montmorillonite K10 in distilled water. In similar to other clay minerals, montmorillonite K10 can absorb water in its interlayer spaces. Through the water adsorption, the layers move apart from together giving the swelled montmorillonite. The swelling expands the surface area of montmorillonite and exposes the cations of interlayers to contribute in Brønsted and Lewis acid properties of the clay mineral [20], ii) preparation of homoionic Na<sup>+</sup>-exchanged montmorillonite by an adequate stirring of the swelled montmorillonite in an

aqueous solution of NaCl. In this sate and through the ion-exchange ability, many cations of interlayers in montmorillonite are exchanged with Na<sup>+</sup> ions. Diffusion of Na<sup>+</sup> ions brings high capacity towards the clay mineral to exchange Na<sup>+</sup> ions with various guest species (transition metals ions/nanoparticles, complexes and H<sup>+</sup> ions) and this is leading to the encapsulation of guest species in interlamellar spaces of the clay mineral. Moreover, by altering the cations of interlayers, the acidity (Brønsted and Lewis) of the clay mineral could be changed for different purposes, and iii) preparation of acid-activated montmorillonite by stirring of homoionic Na<sup>+</sup>-exchanged montmorillonite in an aqueous solution of HCl.

The concentration of exchangeable cations in a clay mineral is called cation-exchange capacity (CEC) and measured as milli-equivalent per 100 g of the dried clay [19]. The measuring resulted that CEC for Mont K10 is 85 meq·g<sup>-1</sup> and for Na<sup>+</sup>-Mont is 110 meq·g<sup>-1</sup>. This is showing that by replacing Na<sup>+</sup> ions instead of other cations in interlamellar spaces, the cation exchange capacity of H<sup>+</sup>-Mont system was raised.



Figure 2. A three-step procedure for preparation of H<sup>+</sup>-Mont clay

### 3.2. FT-IR analysis

Fourier transform infrared spectroscopy as a primarily tool was utilized for structural elucidation of montmorillonite K10 and acid-activated montmorillonite (Figure 3). The illustrated FT-IR spectrum of Mont K10 shows the absorption bands at 3620 and 1635 cm<sup>-1</sup> due stretching and bending vibrations of OH groups bonded to Si, Al and other existed metals. A broad band near 3430 cm<sup>-1</sup> is attributed to H–O–H stretching vibrations of adsorbed water on the surface of montmorillonite, a strong absorption band at 1054 cm<sup>-1</sup> derived from stretching vibration of Si–O bonds in tetrahedral sites, a small absorption band at 795 cm<sup>-1</sup> attributed to the presence of amorphous silica, and the bands at 522 and 464 cm<sup>-1</sup> due bending vibration of Si–O–Al and Si–O–Si bonds. It is notable that although FT-IR spectrum of H<sup>+</sup>-Mont clay shows the same absorption-pattern of montmorillonite K10, however, through the acid-activation, the position of wide stretching vibration band of Si–O (1054 cm<sup>-1</sup>) in Mont K10 was shifted to 1080 cm<sup>-1</sup> showing the successful ion-exchange processing of H<sup>+</sup>-Mont system.



### Wavenumber (cm<sup>-1</sup>)

Figure 3. FT-IR spectra of Mont K10 and H<sup>+</sup>-Mont clay

#### 3.3. SEM and EDX analysis

SEM images and EDX spectra of Mont K10 and acid-activated Mont were illustrated in Figure 4. Comparison of the images (Figure 4a and c) shows that through the acid-activation, the adjacent sheets of Mont K10 are exfoliated to tiny segments. This phenomenon is interpreted by major elimination of  $Al^{3+}$  and  $Fe^{2+/3+}$  contents from octahedral sites while the activation of montmorillonite with HCl was carried out. As well, through the elimination of  $Al^{3+}$  and  $Fe^{2+/3+}$  ions from interlayers, many new pores on the surface and internal layers of montmorillonite are produced leading to raise of surface area in H<sup>+</sup>-Mont system [42]. It was also reported that the rate of metal ions-elimination in a clay mineral depends to the concentration of HCl, temperature and processing time of the activation [43]. The acid-activation at low HCl-concentration seems to cause little damage to the silicate layer affording the platelet-structure of clay-Mont system remains intact. However, the prolonged processing time in acid-activation may result complete delamination leading to the collapse of layers in the clay mineral [44].





**Figure 4.** a) SEM image of Mont K10, b) EDX spectrum of Mont 10, c) SEM image of H<sup>+</sup>-Mont and d) EDX spectrum of H<sup>+</sup>-Mont

#### 3.4. XRD analysis

More investigation towards phase purity and structural elucidation of the clay composite systems was carried out by plotting the broad angel XRD spectrum of the prepared samples (Figure 5). As seen in Figure 5a, montmorillonite K10 possesses a number of sharp peaks corresponding to various impurities (quartz, cristobalite and feldspar) along with hkl and two dimensional hk reflections. Figure 5b also represents that the intensity of absorption peaks in Na<sup>+</sup>-exchanged montmorillonite was significantly increased. This

situation shows that via the ion-exchange ability, Na<sup>+</sup> ions were successful diffused to interlamellar spaces of the clay mineral leading to dramatic raise of Na<sup>+</sup>-occupation [45, 46]. In contrast, Figure 5c shows that the intensity of absorption peaks in H<sup>+</sup>-Mont clay system was notably reduced. This phenomenon is attributed to exfoliation/destruction of layers in Na<sup>+</sup>-Mont system through the acid-activation of Mont K10 with HCl [47].



Figure 5. Broad angle XRD patterns of a) Mont K10, b) Na<sup>+</sup>-Mont and c) H<sup>+</sup>-Mont clays

### 3.5. BET analysis

In order to investigate the porosity and specific surface area of the clay systems, N<sub>2</sub> adsorption–desorption isotherm of Mont K10 and H<sup>+</sup>-Mont clays were illustrated in Figure 6. The plot-analysis shows that the shape of isotherms for the examined clay minerals is similar and according to BDDT classification is adapted to the isotherm of type IV with H3 hysteresis loop. This type of isotherm is a characteristic of micro/meso porous materials [48, 49]. As well, the obtained data for Mont K10 and H<sup>+</sup>-Mont clays represented that the BET surface area and total pore volume of H<sup>+</sup>-Mont system was increased rather than the alone Mont K10 (Table 1). This is attributed to exfoliation/destruction of adjacent layers in Mont K10 to tiny segments by the acid-activation. In addition, via the processing of montmorillonite K10 with hydrochloric acid and elimination of inherent consisted metal ions of octahedral sites, more new pores are generated affording the rise of pore volume and specific surface area in H<sup>+</sup>-Mont system [50, 51].



Figure 6. N₂ adsorption–desorption isotherms of a) Mont K10 and b) H<sup>+</sup>-Mont clays

Table 1. Surface properties of Mont K10 and H <sup>+</sup> -Mont clays						
Samples	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Vm (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)	Vp (cm³g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
Mont K10	250.11	51.835	6.427	0.4016	0.4298	
H⁺-Mont	280.52	50.313	6.7483	0.419	0.5081	

### 3.6. Synthesis of biscoumarins catalyzed by H<sup>+</sup>-Mont system

The literature review shows that synthesis of biscoumarin materials due their wide spread biological activities has attracted the attention of many scientists. In this context, phosphotungstic acid [52], I<sub>2</sub> [53], ZnCl<sub>2</sub> [54], Zn(Proline)<sub>2</sub> [55], sodium dodecyl sulfate (SDS) [56], *n*-dodecylbenzene sulfonic acid (DBSA) [57], *n*-Bu<sub>4</sub>NBr [58], [Et<sub>3</sub>NH][HSO<sub>4</sub>] [59], sulfated titania [60], propane-1,2,3-triyl tris(hydrogen sulfate) [61], sulfonated rice husk ash (RHA-SO<sub>3</sub>H) [62, 63], P4VPy-CuO NPs [64], silica-supported Preyssler NPs [65], silica sulphuric acid NPs [66], silica-bonded *N*-propylpiperazine sodium *n*-propionate [67], silica supported sodium hydrogen sulfate and indion 190 resin [68], mesoporous FeTUD-1 [69], nano Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub>-H<sub>3</sub>PO<sub>4</sub> [70], graphene oxide nanosheets [71], tetramethylguanidium-based ionic liquids [72], task-specific ionic liquids [73], [MIM(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>H][HSO<sub>4</sub>] [74] and SO<sub>3</sub>H-functionalized ionic liquids based on benzimidazolium cation [PSebim][OTf] [75] are some of the catalyst systems which have been successfully served for synthesis of biscoumarins. Although, the mentioned protocols have the own merits or shortcomings, however, introduction of new, efficient and ecologically safe methods is a subject of more interest and is still demanded.

After the successful synthesis and characterization of acid-activated montmorillonite, we therefore prompted to investigate the catalytic activity of the prepared H<sup>+</sup>-Mont clay system towards tandem Knoevenagel-Michael reaction of aromatic aldehydes with 4-hydroxycoumarin under green and more efficient conditions.

The investigation was primarily carried out by performing the condensation reaction of 4-hydroxycoumarin (2 mmol) and 4-chlorobenzaldehyde (1 mmol) in the presence and absence of H<sup>+</sup>-Mont clay under different reaction conditions. The results of this investigation are summarized in Table 2. Observation of the results represented that in the absence of H<sup>+</sup>-Mont clay, the reaction did not show any efficiency (entries 1–3). However, by adding a small amount of H<sup>+</sup>-Mont nanocatalyst, the rate of condensation reaction was dramatically accelerated. More examinations resulted that using 20 mg H<sup>+</sup>-Mont clay per 1 mmol of 4-chlorobenzaldehyde in a mixture of EtOH-H<sub>2</sub>O (1:1) at room temperature was the requirements to afford

Table 2. Optimization experiments for synthesis of biscoumarin 3b catalyzed by H <sup>+</sup> -Mont clay <sup>a</sup>						
Entry	H <sup>+</sup> -Mont (mg)	Solvent (2 mL)	Condition	Time (min)	Yield (%) <sup>b</sup>	
1	-	H <sub>2</sub> O	r.t.	360	10	
2	-	EtOH-H <sub>2</sub> O (1:1)	r.t.	360	10	
3	-	EtOH-H <sub>2</sub> O (1:1)	reflux	120	20	
4	20	H <sub>2</sub> O	r.t.	120	65	
5	20	EtOH-H <sub>2</sub> O (1:1)	r.t.	25	95	
6	30	EtOH-H <sub>2</sub> O (1:1)	r.t.	25	90	
7	10	EtOH-H <sub>2</sub> O (1:1)	r.t.	25	70	
8	20	CH₃CN	r.t.	180	34	
9	20	CH <sub>2</sub> Cl <sub>2</sub>	r.t.	180	20	
<sup>a</sup> The condensation reactions were carried out with 4-hydroxycoumarin (2 mmol) and 4-chlorobenzaldehyde (1 mmol). <sup>b</sup> Isolated vield.						

biscoumarin **3b** in 95% isolated yield (Table 2, entry 5), while the reaction was carried out with 100% conversion.

In continuation, the capability of nano/meso porous H<sup>+</sup>-Mont clay was highlighted by a comparison for synthesis of biscoumarin **3b** catalyzed by H<sup>+</sup>-Mont system versus the parent montmorillonite K10 and other metal ions (Fe<sup>3+</sup>, Al<sup>3+</sup> and Na<sup>+</sup>) exchanged montmorillonites at the optimized reaction conditions (Figure 7 and Table 3). The obtained results represented that the condensation reaction in the presence of Mont K10 and other metal ions exchanged Monts was only progressed up to 75% within 120 min. This is showing that although Mont K10 is naturally acidic clay, however, it exhibited less reactivity towards synthesis of biscoumarin **3b**. In contrast, replacing of protons instead of other metal ions in interlayers of Mont K10 strongly enhances the Brønsted acidity of H<sup>+</sup>-Mont system leading to the perfect efficiency of the titled reaction [76]. Moreover, generation of numerous nano/meso pores on the surface as well as distancing of interlayers in the clay mineral (this is led to dramatic raise of specific surface area) are the reasons which H<sup>+</sup>-Mont clay performs the condensation reaction more easily and with the perfect efficiently.



Figure 7. Comparison of the catalytic activity of Mont K10 and H<sup>+</sup>-Mont clays in synthesis of biscoumarin 3b

Table 3. Synthesis of biscoumarin 3b catalyzed by Mont clays <sup>a</sup>				
Entry	Catalyst	Time (min)	Yield (%) <sup>b</sup>	
1	Mont K10	120	45	
2	Al <sup>3+</sup> -Mont	120	60	
3	Na <sup>+</sup> -Mont	120	50	
5	Fe <sup>3+</sup> -Mont	120	75	
4	H+-Mont	25	95	
<sup>a</sup> The condensation reactions were carried out using 4-hydroxycoumarin (2 mmol), 4-chlorobenzaldehyde (1 mmol) and 20 mg of the clay catalyst in a mixture of EtOH-H <sub>2</sub> O (1:1 mL). <sup>b</sup> Isolated yield.				

At the next, generality and versatility of this synthetic method was more investigated by synthesis of structurally diverse biscoumarin materials through the condensation reaction of 4-hydroxycoumarin and substituted aromatic aldehydes at the optimized reaction conditions. The results of this investigation are

summarized in Table 4. As seen, all reactions were carried out successfully within 25–50 min at room temperature to afford biscoumarins in high to excellent yields.

2
orted
30 [55]
59 [63]
07 [63]
02 [52]
71 [63]
51 [63]
37 [38]
70 [74]
25 [55]
35 [63]
04 [60]
[]

<sup>a</sup> All reactions were carried out with the molar ratio of 1:2 (aromatic aldehyde/4-hydroxycoumarin) in the presence of 20 mg of H<sup>+</sup>-Mont clay at room temperature. <sup>b</sup> Isolated yield.

Although the exact mechanism of this synthetic protocol is not clear, however, a proposed mechanism for synthesis of biscoumarin materials catalyzed by H<sup>+</sup>-Mont clay involves: i) the activation of carbonyl group of aromatic aldehyde with H<sup>+</sup>-Mont clay as a Brønsted acid-catalyst, ii) the Knoevenagel condensation of 4-hydroxycoumarin with the activated aldehyde affords intermediate I, iii) the Michael addition of second molecule of 4-hydroxycoumarin with intermediate I produces intermediate II, and iv) a simple enolization of intermediate II gives the final biscoumarin product (Figure 8).





Figure 8. A proposed mechanism for synthesis of biscoumarins catalyzed by H<sup>+</sup>-Mont clay

The usefulness and capability of H<sup>+</sup>-Mont mesoporous clay in one-pot synthesis of biscoumarin **3b** was highlighted by a comparison of the obtained results with the previously reported catalyst systems (Table 5). A survey shows that in terms of low reaction time, mild reaction conditions, perfect reusability of H<sup>+</sup>-Mont clay and high yield of the product, the present work exhibits more or comparable efficiency than the previous systems.

Table 5. Comparison of the synthesis of biscoumarin 3b with H <sup>+</sup> -Mont clay and other reported catalyst systems						
Entry	Catalyst	Time (min)	Yield (%)	Condition	Reusability	Ref.
1	H*-Mont mesoporous clay	25	95	H <sub>2</sub> O/r.t.	6	*
2	Phosphotungstic acid	20	93	H <sub>2</sub> O/80 °C	5	[52]
3	Molecular iodine	27	93	H <sub>2</sub> O/100 °C	-	[53]
4	Sodium dodecyl sulfate	150	93	H <sub>2</sub> O/60 °C	5	[56]
5	n-Dodecylbenzene sulfonic acid	60	87	H <sub>2</sub> O/40 °C	-	[57]
6	n-Bu₄NBr	30	95	H <sub>2</sub> O/100 °C	-	[58]
7	Sulfated titania	15	96	H <sub>2</sub> O/80 °C	5	[60]
8	RHA-SO <sub>3</sub> H	25	92	Solvent-free/80 °C	-	[63]
9	Silica sulfuric acid NPs	20	92	H <sub>2</sub> O/reflux	-	[66]
10	NaHSO <sub>4</sub> /SiO <sub>2</sub>	30	90	Toluene/100 C	3	[68]
11	nano Fe <sub>3</sub> O <sub>4</sub> @ZrO <sub>2</sub> -H <sub>3</sub> PO <sub>4</sub>	12	97	H <sub>2</sub> O/reflux	4	[70]
12	Graphene oxide nanosheets	15	80	H <sub>2</sub> O/reflux	4	[71]
13	[PSebim][OTf] as IL (ionic liquid)	120	96	IL/70 °C	2	[75]
* Present work						

#### 3.7. Reusability of H<sup>+</sup>-Mont clay

For industrial and practical purposes, recyclability of the applied catalyst is a subject of more interest. This issue was investigated through the synthesis of biscoumarin **3b** in the presence of H<sup>+</sup>-Mont clay as a model reaction. After completion of the reaction at the first run, the clay nanocatalyst was separated, washed with ethanol and then dried for reusing at the next runs. The model reaction was again charged with the fresh solvent, starting materials and the recovered H<sup>+</sup>-Mont clay. Figure 9 shows that the H<sup>+</sup>-Mont nanocatalyst can be reused for six consecutive cycles without the significant loss of catalytic activity.



Figure 9. Reusability of H<sup>+</sup>-Mont clay for synthesis of biscoumarin 3b

### Conclusion

In this study, the mesoporous acid-activated montmorillonite (H<sup>+</sup>-Mont) was easily prepared and then characterized using FT-IR, SEM, EDX, XRD and BET analyses. The prepared Brønsted acid nanocatalyst showed a perfect catalytic activity towards tandem Knoevenagel-Michael reaction of various aromatic aldehydes with 4-hydroxycoumarin. All reactions were carried out at room temperature in a mixture EtOH- $H_2O$  (1:1) to afford biscoumarin materials within 20–50 min. H<sup>+</sup>-Mont as a heterogeneous clay catalyst was easily separated from the reaction mixture and reused for 6 consecutive cycles without the significant loss of catalytic activity. This synthetic protocol offers numerous advantages in terms of easy synthesis of nano/mesoporous H<sup>+</sup>-Mont clay system, mild reaction conditions, using a mixture of H<sub>2</sub>O-EtOH as green solvent, short reaction times, high yield of the products, simple work-up procedure and the great reusability of the nanocatalyst.

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# Strongly proton exchanged montmorillonite K10 (H<sup>+</sup>-Mont) as a solid acid catalyst for highly efficient and environmental benign synthesis of biscoumarins via tandem Knoevenagel-Michael reaction

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In this study, the mesoporous acid-activated montmorillonite (H<sup>+</sup>-Mont) was easily prepared and then characterized using FT-IR, SEM, EDX, XRD and BET analyses. The prepared Brønsted acid nanocatalyst showed a perfect catalytic activity towards tandem Knoevenagel-Michael reaction of various aromatic aldehydes with 4-hydroxycoumarin. All reactions were carried out at room temperature in a mixture EtOH- $H_2O$  (1:1) to afford biscoumarin materials within 20–50 min.

