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Efficient one-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones catalyzed by a new heterogeneous catalyst based on Co-functionalized Na⁺-montmorillonite†

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In the present study, we report a simple, facile and efficient solvent-free protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones by the three component condensation of aldehyde, ethyl acetoacetate and urea through using Co@imine-Na⁺-MMT as a new, environmentally friendly and reusable heterogeneous catalyst. The structure of the synthesized catalyst was characterized by various techniques, including IR, SEM, TGA, EDX, AAs, DR-UV-vis and XRD analyses. Green reaction conditions, high quantitative yields and the easy isolation of products, easy separation and recovery of the catalyst and short reaction times are some of the advantages of our procedure.

1. Introduction

Montmorillonite (MMT) is one of the phyllosilicate minerals that has received considerable attention due to its unique features such as layered structure, large surface area, thermal and mechanical stability and high ion-exchange capacity. To date, montmorillonite has been used in various fields such as pharmaceuticals, decolorizing agents and supported catalysts.[1–7] The building blocks of this kind of clay consist of a central octahedral aluminum sheet $[Al(OH_6)^{3-}]$ sandwiched by two tetrahedral sheets of silica $(Si_2O_5{}^{2-})$.[8] As a result of these structural features, a permanent negative charge develops in the MMT layers, which is normally balanced by alkali or earth alkaline cations such as Na⁺, K⁺, and Ca²⁺.[9] Normally, montmorillonite layers have a thickness of approximately 1 nm and lateral dimensions of about 30 nm.[10] Generally, broken bonds on the edge of the layered silicate lead to the formation of hydroxyl groups, which can be functionalized to admit catalyst moieties.[11–13] For example, Shirini *et al.* reported the synthesis of 4,4-(arylmethylene)-bis-(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) derivatives in the presence of Na⁺-MMT-[pmim]HSO₄.[14] Also, Sarvi *et al.* have presented syntheses of different xanthenes and coumarins in the presence of AHS@MMT.[15]

Dihydropyrimidinones (DHPMs) are an outstanding class of heterocyclic compounds. Many properties, such as

antibacterial, antioxidant, anti-HIV and anticancer activities have been reported for these compounds.[16,17] Hitherto, various derivatives of these structural motifs have exhibited calcium channel modulatory effect in treatment of cardiovascular diseases.[18] 3,4-Dihydropyrimidin-2(1*H*)-ones can be prepared by one-pot condensation of an aldehyde, β-ketoester and urea under strongly acidic conditions.[19] The multicomponent Biginelli reaction can proceed in the presence of Ln(OTf)₃,[20] NiCl₂·5H₂O,[21] Fe(OTs)₃·6H₂O,[22] Bi(NO₃)₃,[23] Fe(OTs)₃·6H₂O,[24] Fe₃O₄ NPs,[25] Mn(OAc)₃·2H₂O,[26] *p*-dodecylbenzenesulfonic acid,[27] bakers' yeast,[28] (NH₄)₂CO₃,[29] silica sulfuric acid,[30] sulfated tungstate,[31] Cu(OTf)₂,[32] CD-SO₃H,[33] FeCl₃·6H₂O[34] IRMOF-3,[35] chiral phosphoric acid,[36] bentonite/PS-SO₃H,[37] Ce(LS)₃,[38] NH₄OAc[39] as a catalyst. Although these strategies provide an improvement in the preparation of these heterocyclic molecules, some of these methods suffer from such disadvantages as harsh reaction conditions, the need for excess amounts of the catalyst, the use of toxic organic solvents, low yield and prolonged reaction time. Therefore, investigations for development of more efficient, simpler, and milder procedures to overcome these problems are still required (Scheme 1).

2. Experimental
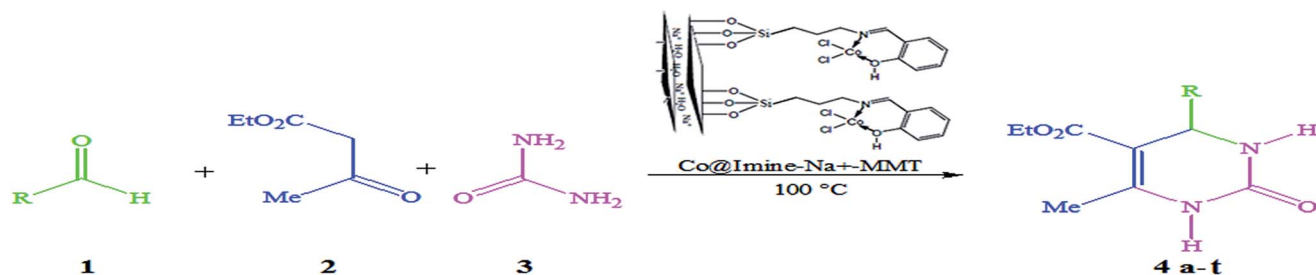
2.1. Material and method

Chemical reagents in high purity were purchased from Fluka or Merck and Southern Clay Products companies. 3-Aminopropyltriethoxysilane (APTES) with 99% purity, 2-hydroxybenzaldehyde with 99.9% purity and dichloromethane with 99.8% purity were bought from Sigma-Aldrich, USA. Toluene

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Scheme 1 One-pot three-component reaction of different aldehydes, ethyl acetoacetate and urea catalyzed by Co@imine-Na$^+$-MMT nanocatalyst.

was purchased from Shanghai Experiment Reagent Co., Ltd (Shanghai, China).

2.1.1. Functionalization of Na$^+$-MMT with 3-aminopropyltriethoxysilane (APTES@Na$^+$-MMT). Na$^+$-MMT (2 g) was dispersed in dry toluene (50 mL) by sonication for 40 min, and then 3-aminopropyltriethoxysilane (APTES, 4 mL) was introduced to the above-mentioned solution. The mixture was refluxed for 24 h under nitrogen atmosphere. After 24 h, the functionalized Na$^+$-MMT (APTES@Na$^+$-MMT) was filtered and washed thoroughly, using the mixture of H$_2$O/ethanol and APTES@Na$^+$-MMT dried under vacuum oven.
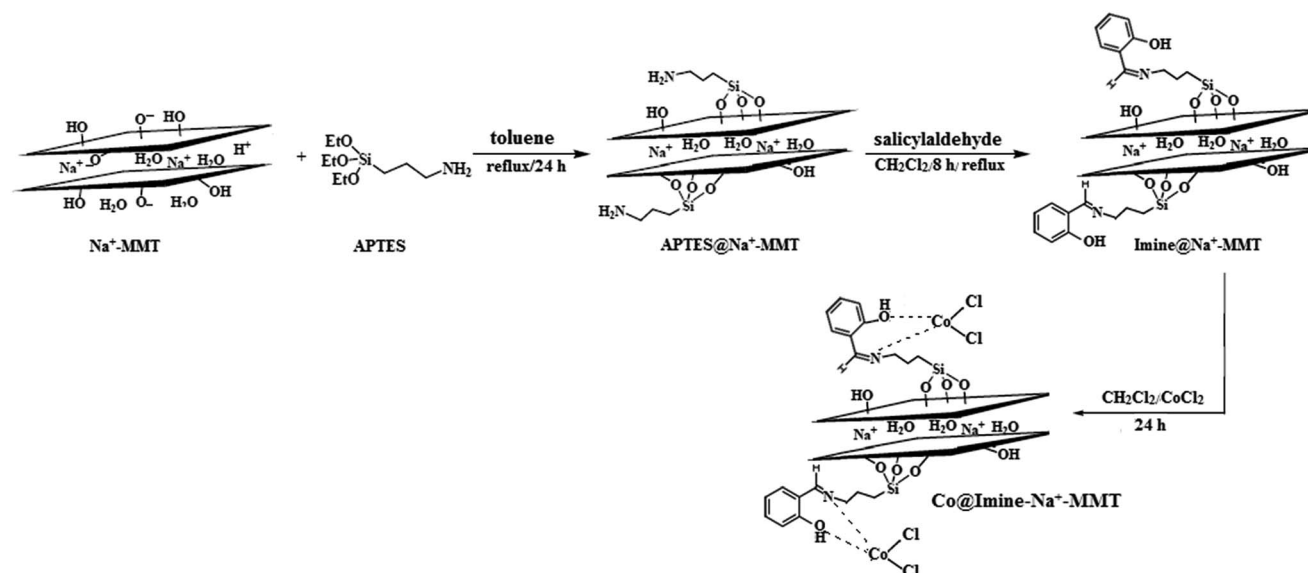
2.1.2. Preparation of imine@Na$^+$-MMT. To prepare imine@Na$^+$-MMT, APTES@Na$^+$-MMT (2 g) was dispersed in 20 mL of CH$_2$Cl$_2$ for 30 min. Subsequently, salicylaldehyde (0.245 g) was added to the reaction mixture and the mixture was refluxed for 8 h. Finally, imine@Na$^+$-MMT was separated by filtration, washed with water (20 mL), and then dried under vacuum oven. Amount of N in the imine@Na$^+$-MMT was 2.3 wt%.

2.1.3. Preparation of Co@imine-Na$^+$-MMT. Two g of imine@Na$^+$-MMT was suspended in CH$_2$Cl$_2$ (20 mL). Afterwards, CoCl$_2$ (0.25 mmol) was added to 10 mL of CH$_2$Cl$_2$, and the reaction mixture was stirred for 24 h under a nitrogen

atmosphere. After 24 h, Co@imine-Na$^+$-MMT was separated by filtration, and the product was washed with water to remove unreacted metal precursors. Amount of N in the Co@imine-Na$^+$-MMT was 1.7 wt%. All stages of the Co@imine-Na$^+$-MMT synthesis is shown in Scheme 2.

2.2. Instrumental measurements

The purity determination of the product and reaction monitoring were carried out by TLC on silica gel 60 F254 (0.25 mm thick). NMR spectra were measured by a Bruker DRX-400 AVANCE spectrometer (^{1}H NMR: 400 MHz; ^{13}C NMR: 100 MHz). FTIR spectra were obtained in KBr pallets on a Perkin-Elmer PXI spectrometer. The low- and broad-angle X-ray diffraction (XRD) measurements were recorded in the 2θ range of 2–80° at room temperature on a Philips X-pert diffractometer (Holland), using Ni-filtered Co-Kα radiation ($\lambda = 1.54$ Å). Scanning election microphotograph (SEM-EDX) was carried out on a SEM-Philips XL30. Thermogravimetric analyses (TGA) were performed at the temperature ranging from room temperature to 700 °C in a nitrogen flow by using a Linseis SATPT instrument. Diffuse reflection spectroscopy was

Scheme 2 All stages of the Co@imine-Na$^+$-MMT synthesis.

recorded on a Sinco S4100, Korea. Elemental analyses were done, using a Carlo-Erba EA1110CNNO-S analyzer and agreed (within 0.30) with the calculated values.

3. Results and discussion

3.1. Synthesis and characterization of catalyst

3.1.1. IR analysis of Co@imine-Na⁺-MMT. The corresponding FT-IR spectra of the pure Na⁺-MMT, APTES@Na⁺-

MMT, imine@Na⁺-MMT and Co@imine-Na⁺-MMT samples in the region of 400–4000 cm^{-1} are presented in Fig. 1. In the case of pure Na⁺-MMT, the absorption peak at 3632 cm^{-1} is related to the free hydroxyl units bonded to the aluminum or magnesium; however the peaks appearing in the 3441 and 1638 cm^{-1} region can be attributed to the OH stretching vibration of the adsorbed water. The bands at 1044 and 918 cm^{-1} are collectively attributed to Si–O stretching vibrations. In the case of APTES@Na⁺-MMT, the observed peaks at 1636 and 3437 cm^{-1}
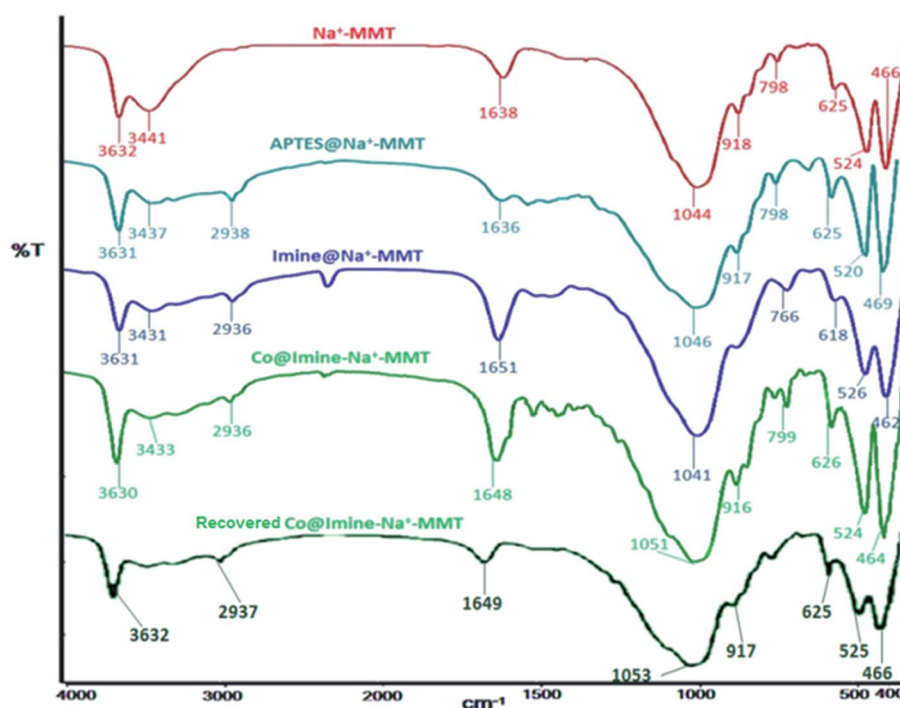

Fig. 1 FTIR spectra of Na⁺-MMT, APTES@Na⁺-MMT, imine@Na⁺-MMT, Co@imine-Na⁺-MMT and recovered Co@imine-Na⁺-MMT.
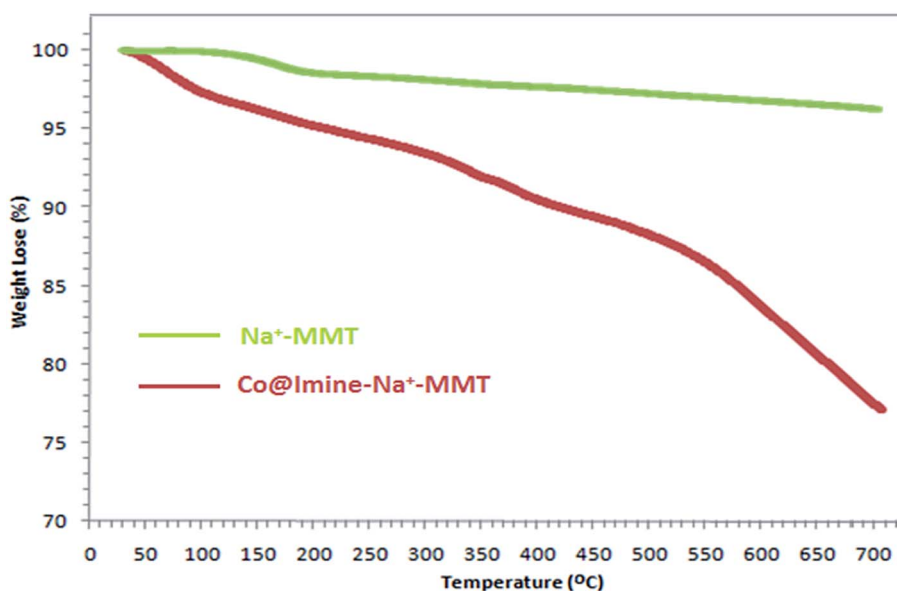

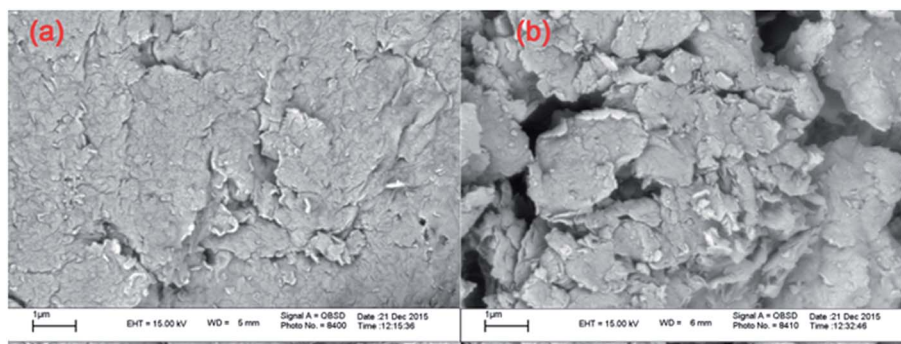**Fig. 2** TGA curves of Na⁺-MMT and Co@imine-Na⁺-MMT.

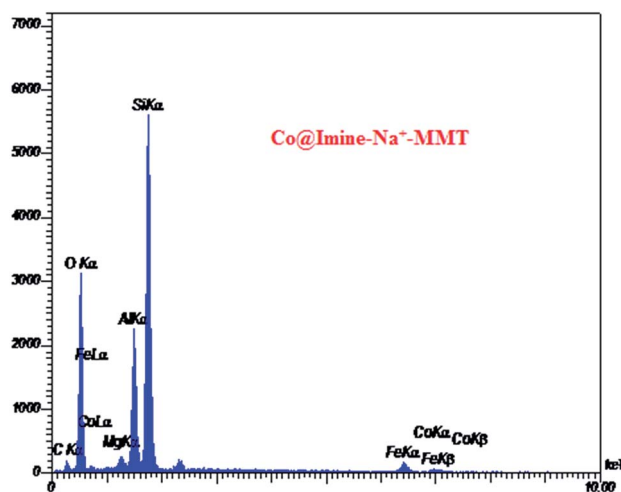Fig. 3 SEM images of Na$^+$-MMT (a) and Co@imine-Na$^+$-MMT (b).

Fig. 4 The energy-dispersive X-ray spectroscopy (EDX) of the Co@imine-Na$^+$-MMT.

are assigned to the –NH$_2$ bending and stretching vibrations, respectively. In addition, the absorption peaks at 2938 cm^{-1} are assigned to the C–H stretching vibrations of propyl groups of APTES. The bands at 1400–1500 cm^{-1} in the imine@Na$^+$-MMT

are related to the aromatic C=C stretching while the absorption peak in the 1651 cm^{-1} region can be assigned to the C=N double bond. The shift of absorption band related to the C=N band from 1651 cm^{-1} in imine@Na$^+$-MMT to 1648 cm^{-1} in Co@imine-Na$^+$-MM confirms the coordination of Schiff base ligand. Furthermore, the spectra of the Co@imine-Na$^+$-MM and recovered Co@imine-Na$^+$-MMT were compared. The spectra are virtually identical which confirm the fine reusability of the catalyst.

3.1.2. Thermal studies of Co@imine-Na$^+$-MM. The TG curve of Na$^+$-MMT displays a weight loss of approximately 8% up to a temperature of 150 °C which is concerned with the loss of the physically adsorbed water. Additionally, there is a slight weight loss between 150 and 600 °C, probably corresponding to the breaking of the bonded H$_2$O within the gallery. TGA of Co@imine-Na$^+$-MMT illustrates approximately 9% weight loss up to 330 °C due to the adsorbed water in the clay. Furthermore, the second weight loss (15%) appearing at 350 °C is associated with the decomposition of the anchored alkyl chain of imines (Fig. 2).

3.1.3. SEM analysis of Co@imine-Na$^+$-MM. Scanning electron microscopy (SEM) was investigated to determine the morphology and size details, as shown in Fig. 3a and b. The SEM images for the catalysts clearly showed variations in the
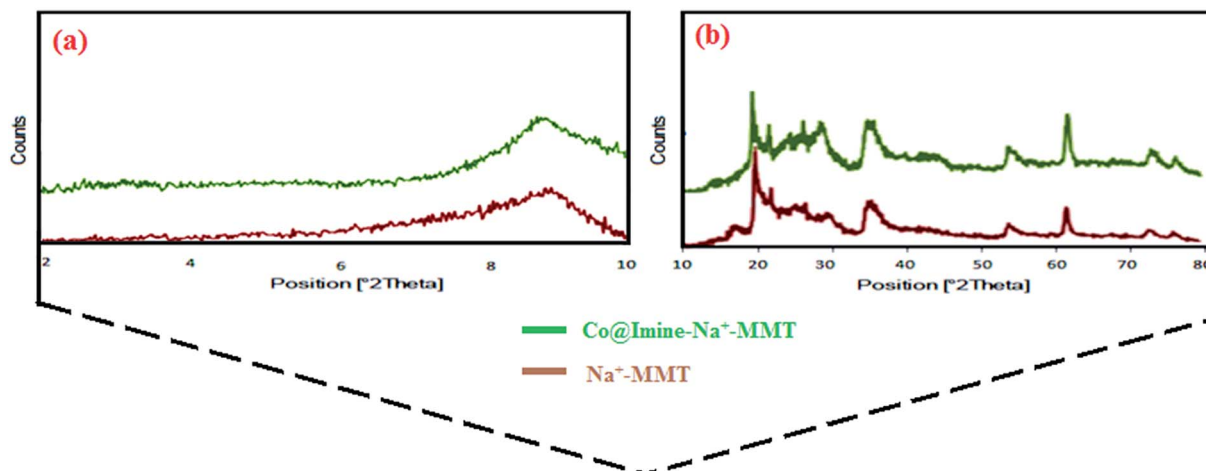

Fig. 5 XRD patterns of the Na$^+$-MMT and Co@imine-Na$^+$-MMT.
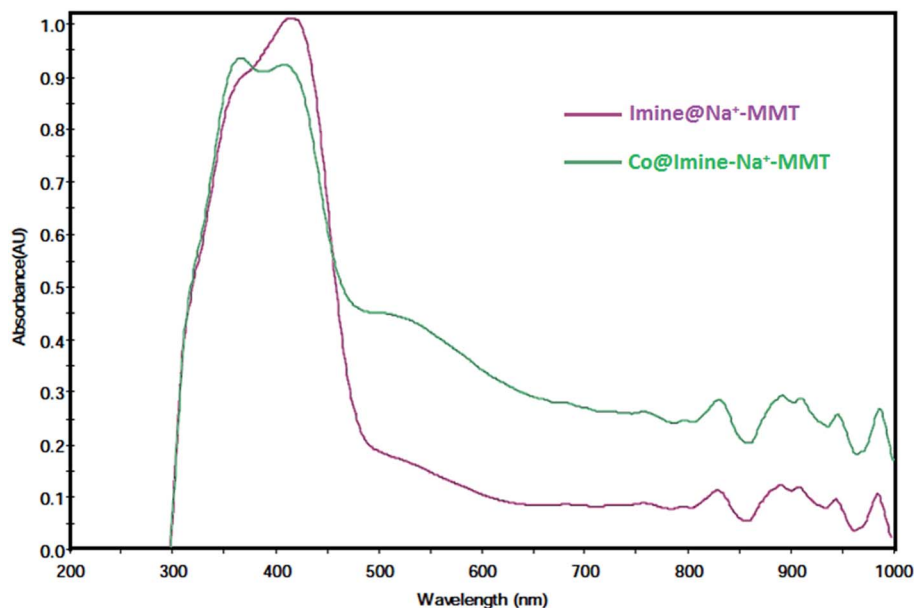
Fig. 6 Diffuse reflectance spectroscopy (DRS) of Na^+-MMT and Co@imine-Na^+-MMT.

surface of these nanoparticles. In the case of Co@imine-Na^+-MMT with disappearance of the lumpy shape of Na^+-MMT, some layers were formed as a uniform structure, which could be attributed to the anchoring of the organic and metal groups. According to Fig. 3b, Co@imine-Na^+-MMT has flaky shapes with nano dimension of 40–50 nm in size.

3.1.4. EDX analysis of Co@imine-Na^+-MMT. The chemical identity of the Co@imine-Na^+-MMT nanoparticles was corroborated by EDX analysis (Fig. 4). The EDX analysis of the nanocatalysts indicated expected elements such as Fe, Mg, Al, C, O and Co of Co@imine-Na^+-MMT. In addition, the Co content of the nanoparticles was determined to be about 0.5 wt% by the atomic absorption spectroscopy (AAS) analysis.

3.1.5. XRD analysis of Co@imine-Na^+-MMT. Fig. 5a displays the low-angle XRD (X-ray diffraction) patterns of the Na^+-MMT used, and Co@imine-Na^+-MMT to illustrate the changes in the distance between the montmorillonite layers (d_{001}). The interlayer distance in the Na^+-MMT (11.42 Å) increases in the course of chemical modifications up to 12.45 Å for Co@imine-Na^+-MMT. This change can point that Co species are intercalated into the interlayer of montmorillonite with the assistance of the organic groups. Additionally, comparison of the broad-angle X-ray diffraction patterns of Na^+-MMT and Co@imine-Na^+-MMT demonstrates that peak patterns of Na^+-MMT were preserved (Fig. 5b). This clearly shows that the crystalline structure and morphology of the montmorillonite nanoparticles remained intact upon organic functionalization

Table 1 Optimization of the reaction conditions in different solvents[a]

Entry	Solvent	Amount of catalyst (mg)	Temperature (°C)	Reaction time (min)	Yield[b] (%)
1	—	—	100	60	—
2	—	5	100	10	90
3	—	10	100	10	96
4	—	15	100	10	94
5	H_2O	10	Reflux/100 °C	30	49
6	EtOH	10	Reflux/78 °C	30	82
7	DMF	10	Reflux/153 °C	30	38
8	DMSO	10	Reflux/189 °C	30	42
9	CH_2Cl_2	10	Reflux/40 °C	30	40
10	$CHCl_3$	10	Reflux/61 °C	30	41
11	Toluene	10	Reflux/110 °C	30	76
12	—	10	—	10	35
13	—	10	80	10	85
14	—	10	90	10	92

[a] Reaction conditions: a mixture of 4-nitrobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol) and Co@imine-Na^+-MMT (10 mg).
[b] Isolated yield.

Table 2 The Co@imine-Na$^+$-MMT catalyzed three-component Biginelli coupling^a

Entry	R	Yield^b (%)	Time (min)	Mp^c (°C) found	Mp (°C) (Lit)
4a	C$_6$H$_5$–	92	10	203–204	202–203 (ref. 44)
4b	2-(NO$_2$)–C$_6$H$_4$–	94	10	219–221	220–222 (ref. 26)
4c	3-(NO$_2$)–C$_6$H$_4$	94	10	225–226	226–228 (ref. 44)
4d	4-(NO$_2$)–C$_6$H$_4$–	96	10	209–211	208–211 (ref. 50)
4e	2-(Cl)–C$_6$H$_4$–	95	10	216–218	215–218 (ref. 24)
4f	3-(Cl)–C$_6$H$_4$–	94	10	192–194	192–193 (ref. 35)
4g	4-(Cl)–C$_6$H$_4$–	95	10	212–214	212–214 (ref. 21)
4h	2,4-(Cl)$_2$–C$_6$H$_3$–	96	10	251–253	251–252 (ref. 47)
4i	3,4-(Cl)$_2$–C$_6$H$_3$–	94	10	222–224	222–223 (ref. 49)
4j	4-(F)–C$_6$H$_4$–	93	10	177–179	175–177 (ref. 19)
4k	4-(CF$_3$)–C$_6$H$_4$–	95	10	176–178	173–175 (ref. 45)
4l	3-(Br)–C$_6$H$_4$–	91	10	185–188	185–186 (ref. 48)
4m	2-(HO)–C$_6$H$_4$–	91	10	199–200	199–201 (ref. 46)
4n	4-(HO)–C$_6$H$_4$–	92	10	230–232	231–233 (ref. 44)
4o	2-(OCH$_3$)–C$_6$H$_4$–	93	10	259–261	259–260 (ref. 30)
4p	3-(OCH$_3$)–C$_6$H$_4$–	91	10	207–209	207–208 (ref. 23)
4q	4-(OCH$_3$)–C$_6$H$_4$–	93	10	202–204	203–204 (ref. 44)
4r	3,4-(OCH$_3$)$_2$–C$_6$H$_3$–	91	10	173–176	174–176 (ref. 49)
4s	3-(CH$_3$O)–4-(HO)–	91	10	232–234	233–235 (ref. 44)
4t	4-(CH$_3$)–C$_6$H$_4$–	92	10	215–217	216–217 (ref. 45)

^{a} Reaction conditions: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol) and Co@imine-Na$^+$-MMT (10 mg), 100 °C. ^{b} Isolated yield. ^{c} Melting points are uncorrected.

as well as metal complex formation in Na$^+$-MMT. It should be noted that no peak dedicated to Co species appeared in the patterns of Co@imine-Na$^+$-MMT compared those of Na$^+$-MMT, probably due to the tiny size of Co species.

3.1.6. DR-UV-vis analysis of Co@imine-Na$^+$-MMT. Diffuse Reflectance Spectra (DRS) of imine@Na$^+$-MMT and Co@imine-Na$^+$-MMT was obtained (Fig. 6), and a comparison between them revealed that the foundation remains unchanged during the metal anchoring process.

3.2. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones in the presence of Co@imine-Na$^+$-MMT

A mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), and Co@imine-Na$^+$-MMT (8 mg) was stirred at 100 °C under solvent-free conditions. After the completion of the reaction (monitored by TLC), EtOH (10 mL) was added to the mixture, and the catalyst was filtered off. The pure product was achieved *via* recrystallization from ethanol. The structures of

the products were characterized by the comparison of their melting points, and NMR spectroscopic data with those of the related literature.

In continuation of our efforts to perform organic transformations with the aid of green synthetic methodologies,[40–43] we decided to survey the synthesis of dihydropyrimidin-2(1H)-one compounds with diverse substituents from the reaction of ethyl acetoacetate, aldehyde and urea under solvent-free conditions by using Co@imine-Na$^+$-MMT as a novel, eco-friendly, reusable and promising nanocatalysts.

In order to optimize the reaction conditions for the synthesis of 3,4-dihydro-5-etoxycarbonyl-4-(4-nitrophenyl)-6-methylpyr-imidine-2(1H)-one (**4d**), a systematic study, which considered different variables affecting the reaction yield, was conducted in the reaction of ethyl acetoacetate, 4-nitrobenzaldehyde, and urea (molar ratio 1 : 1 : 1.2) as the model reaction. The results are indicated in Table 1. The primary optimization results showed that the ambient of the catalyst was not suitable to

Table 3 Comparison the results of the synthesis of 3,4-dihydro-5-etoxycarbonyl-4-(4-phenyl)-6-methylpyrimidine-2(1H)-one using different catalysts

Entry	Catalyst and conditions	Reaction time (h)	Yield (%)	Ref.
3	BF$_3$·OEt$_2$/CuCl/THF/reflux	18	71	23
1	Silica sulfuric acid/EtOH/heat	6	91	30
2	Sulfated tungstate/solvent-free/80 °C	1	92	31
4	Cu(OTf)$_2$/EtOH/100 °C/MW	1	95	32
5	CD-SO$_3$H/solvent-free/80 °C	2	89	33
8	IRMOF-3/solvent-free/reflux	5	89	34
9	Chiral phosphoric acid/CH$_2$Cl$_2$/25 °C	4 days	77	36
12	SnCl$_2$-nano SiO$_2$/EtOH/reflux	40 min	92	51
13	Co@imine-Na$^+$-MMT/solvent-free/100 °C	10 min	92	This work

Fig. 7 Reusability of the Co@imine-Na$^+$-MMT.

did not considerably affect the duration of the reaction and the product yield (entries 2 and 4). However, the trial reaction in the presence of solvents such as H_2O, EtOH, DMF, DMSO, CH_2Cl_2, $CHCl_3$, and toluene acquired the desired product **4d** in good to moderate yields but at long reaction times in compared to the solvent-free conditions (entries 5–11). Among the surveyed solvents, using EtOH improved the yield of the chemical reaction under study (entry 6). Moreover, to determine the role of catalysts and temperature under solvent-free conditions, the reaction was surveyed with and without heating with the same amount of catalysts (10 mg) (entries 12–14). It was observed that the use of heating leads to faster reaction and a higher yield.

In order to generalize the effectiveness and the acceptability of the optimum conditions, a variety of appropriate aldehydes (**2a–t**) were selected for the reaction with ethyl acetoacetate (**1**) and urea (**3**); in addition, the desired products were obtained in good-to-excellent yields without problems which may be related to the use of solvents such as pollution, handling and safety. The optimized results are listed in Table 2. It was found that aromatic aldehydes containing both electron-withdrawing (entries 2–13) and electron-donating groups (entries 15–19) showed pretty good reactivity with the ethyl acetoacetate and urea under the optimized reaction conditions.

Furthermore, to illustrate the catalytic efficiency and the capability of Co@imine-Na$^+$-MMT, Table 3 compares our results

formation of the desired product **4d** under solvent-free conditions even at 100 °C (entry 1). In the next phase of study, systematic screening of the reaction conditions was evaluated in the presence of different catalyst amounts (entries 2–4). After several screening experiments with different amounts of catalysts, it was proved that the reaction in the presence of 10 mg of the catalysts under solvent-free conditions resulted in the corresponding product **4d** in the highest yield (entry 3). Increasing and decreasing the amount of catalysts required for the reaction

Scheme 3 The proposed mechanism for the synthesis dihydropyrimidin-2(1H)-ones in the presence of Co@imine-Na$^+$-MMT.

in the synthesis of 3,4-dihydro-5-etoxycarbonyl-4-(4-phenyl)-6-methylpyrimidine-2(1H)-one (4a) with those of other methodologies which have employed other earlier homogeneous and heterogeneous catalysts. It is crystal clear that a suitable methodology in terms of product yield, reaction time, and especially catalyst amount has been developed.

In the next phase of the survey, to check the recovery and reuse cycle of the catalyst, the reaction of 4-nitrobenzaldehyde, ethyl acetoacetate and urea under the optimized reaction conditions was selected as a model reaction. After separating and washing the retained catalyst with ethanol, the above-mentioned solvent was evaporated, and the catalyst was dried and reused for the same reactions. This process was performed over five periods, and all reactions led to the desired products with negligible change in terms of the reaction time and yield, obviously showing the practical recyclability of this catalyst (Fig. 7). However, the yield of product was reduced from 96% to 94% after the 5th run.

A reasonable pathway for the reaction of ethyl acetoacetate, aldehyde, and urea or thiourea conducted in the presence of Co@imine-Na$^+$-MMT is presented in Scheme 2. Due to the 3d empty orbital in the cobalt ion, the activated aldehyde (2), and ethyl acetoacetate (1) can be created through a coordinative bond and stabilized by cobalt. The dihydropyrimidin-2(1H)-one synthesis probably begins via initial formation of the acylimine intermediate (5) by nucleophilic addition of urea (3) to the activated aldehyde (2). The resulting adduct (5) undergoes dehydration to give the complex (6). In this stage, activated ethyl acetoacetate (1) attacks the complex (6). Furthermore, an open-chain ureide (7) is created which undergoes intramolecular cyclization to afford the final product (4) (Scheme 3).

4. Conclusions

In conclusion, we have introduced a simple, facile, and efficient protocol for the synthesis of a wide range of biologically and pharmacologically 3,4-dihydropyrimidin-2(1H)-ones in the presence of Co@imine-Na$^+$-MMT as a new, environmentally friendly and reusable heterogeneous catalyst via a one-pot Knoevenagel condensation of aldehyde, ethyl acetoacetate and urea under solvent-free conditions.

References

1 K. Majdzadeh-Ardakani, A. H. Navarchian and F. Sadeghi, *Carbohydr. Polym.*, 2010, **79**, 547.

2 S. Kantevari, S. V. N. Vuppalapati and L. Nagarapu, *Catal. Commun.*, 2007, **8**, 1857.

3 J. S. Yadav, B. V. S. Reddy, B. Eeshwaraiah and M. Srinivas, *Tetrahedron*, 2004, **60**, 1767.

4 B. S. Kumar, A. Dhakshinamoorthy and K. Pitchumani, *Catal. Sci. Technol.*, 2014, **4**, 2378.

5 F. Shirini, M. Mamaghani and S. V. Atghia, *Catal. Commun.*, 2011, **12**, 1088.

6 D. S. Tong, C. H. Zhou, M. Y. Li, W. H. Yu, J. Beltramini, C. X. Lin and Z. P. Xu, *Appl. Clay Sci.*, 2010, **48**, 569.

7 D. Zhang, C. H. Zhou, C. X. Lin, D. S. Tong and W. H. Yu, *Appl. Clay Sci.*, 2010, **50**, 1.

8 *Crystal Structures of clay and their X-ray identification, Monograph*, ed. G. W. Brindly and G. Brown, Mineralogical Society, London, 1980, pp. 125–195.

9 E. P. Giannelis, R. Krishnamoorti and E. Manias, *Adv. Polym. Sci.*, 1999, **118**, 108.

10 M. Okamoto, S. Mallapragada and B. Narasimhan, Biodegradable Polymer/Layered Silicate Nanocomposites: a review, *Handbook of Biodegradable Polymeric Materials and Their Applications*, American Scientific Publishers, Valencia, California, 2005, pp. 1–45.

11 H. Shi, T. Lan and T. Pinnavaia, *Chem. Mater.*, 1996, **8**, 1584.

12 S. Yariv and H. Cross, in *Clays and Clay Minerals*, ed. M. Dekker, New York, 2002, pp. 463–566.

13 O. Ozdemir, B. Armagan, M. Turan and M. S. Celik, *Dyes Pigm.*, 2004, **62**, 49.

14 F. Shirini, M. Seddighi, M. Mazloumi, M. Makhsous and M. Abedini, *J. Mol. Liq.*, 2015, **208**, 291.

15 S. Sarvi-Beigbaghlou, K. Marjani, A. Habibi and S. V. Atghia, *RSC Adv.*, 2016, **6**, 20306.

16 C. O. Kappe, *Eur. J. Med. Chem.*, 2000, **35**, 1043.

17 S. S. Kim, B. S. Choi, J. H. Lee, K. K. Lee, T. H. Lee, Y. H. Kim and S. Hyunik, *Synlett*, 2009, 599.

18 K. S. Atwal, B. N. S. Wanson, S. E. Unger, D. M. Floyd, S. Mereland, A. Hedberg and B. C. J. O'Reilly, *Med. Chem.*, 1991, **34**, 806.

19 P. G. Biginelli, *Gazz. Chim. Ital.*, 1893, **23**, 360.

20 Y. Huang, F. Yang and C. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 16386.

21 U. B. More, *Asian J. Chem.*, 2012, **24**, 1906.

22 J. T. Starcevich, T. J. Laughlin and R. S. Mohan, *Tetrahedron Lett.*, 2013, **54**, 983.

23 M. M. Khodaei, A. R. Khosropour and M. Beygzadeh, *Synth. Commun.*, 2004, **34**, 1551.

24 C. O. Kappe, D. Kumar and R. S. Varma, *Synthesis*, 1999, **10**, 1799.

25 M. N. Esfahani, S. J. Hoseini and F. Mohammadi, *Chin. J. Catal.*, 2011, **32**, 1484.

26 K. A. Kumar, M. Kasthuraiah, C. S. Reddy and C. D. Reddy, *Tetrahedron Lett.*, 2001, **42**, 7873.

27 M. A. Bigdeli, G. Gholami and E. Sheikhhosseini, *Chin. Chem. Lett.*, 2011, **22**, 903.

28 A. Kumar and R. A. Maurya, *Tetrahedron Lett.*, 2007, **48**, 4569.

29 F. Tamaddon, Z. Razmi and A. A. Jafari, *Tetrahedron Lett.*, 2010, **51**, 1187.

30 P. Salehi, M. Dabiri, M. A. Zolfigol and M. A. B. Fard, *Tetrahedron Lett.*, 2003, **44**, 2889.

31 S. D. Salim and K. G. Akamanchi, *Catal. Lett.*, 2011, **12**, 1153.

32 S. Asghari, M. Tajbakhsh, B. Jafarzadeh-Kenari and S. Khaksar, *Chin. Chem. Lett.*, 2011, **22**, 127.

33 M. Zeinali-Dastmalbaf, A. Davoodnia, M. M. Heravi, N. Tavakoli-Hoseini, A. Khojastehnezhad and H. A. Zamani, *Bull. Korean Chem. Soc.*, 2011, **32**, 656.

34 S. Rostamnia and A. Morsali, *RSC Adv.*, 2014, **4**, 10514.

35 J. Lu and H. Ma, *Synlett*, 2000, 63.

36 X.-H. Chen, X.-Y. Xu, H. Liu, L.-F. Cun and L.-Z. Gong, *J. Am. Chem. Soc.*, 2006, **128**, 14802.

37 R. Javad-Kalbasi, A. R. Massah and B. Daneshvarnejad, *Appl. Clay Sci.*, 2012, **55**, 1.

38 Y. Qiu, H. Sun, Z. Ma and W. Xia, *J. Mol. Catal. A: Chem.*, 2014, **392**, 76.

39 E. Ramu, V. Kotra, N. Bansal, N. Bansal, R. Varala and S. R. Adapa, *J. Chem*, 2008, **1**, 188.

40 K. Rad-Moghadam, S. C. Azimi and E. Abbaspour-Gilandeh, *Tetrahedron Lett.*, 2013, **54**, 4633.

41 E. Abbaspour-Gilandeh, M. Aghaei-Hashjin, A. Yahyazadeh and H. Salemi, *RSC Adv.*, 2016, **6**, 55444.

42 E. Abbaspour-Gilandeh, S. C. Azimi and A. Mohammadi-Barkchai, *RSC Adv.*, 2014, **4**, 54854.

43 E. Abbaspour-Gilandeh and S. C. Azimi, *Iran. Chem. Commun.*, 2015, **3**, 218.

44 R. Ghosh, S. Maiti and A. Chakraborty, *J. Mol. Catal. A: Chem.*, 2004, **217**, 47.

45 Y. Ma, C. Qian, L. Wang and M. Yang, *J. Org. Chem.*, 2000, **65**, 3864.

46 D. Russowsky, F. A. Lopes, V. S. S. Silva, K. F. S. Canto, M. G. Montes and M. N. Godoi, *J. Braz. Chem. Soc.*, 2004, 165.

47 A. D. Patil, N. V. Kumar, W. C. Kokke, M. F. Bean, A. J. Freyer, C. D. Brossi, S. Mai, A. Truneh, D. J. Faulkner, B. Carte, A. L. Breen, R. P. Hertzberg, R. K. Johnson, J. W. Westly and B. C. M. Potts, *J. Org. Chem.*, 1995, **60**, 1182.

48 N. S. Nandurkar, M. J. Bhanushali, M. D. Bhor and B. M. Bhanage, *J. Mol. Catal. A: Chem.*, 2007, **271**, 14.

49 J. S. Yadav, B. V. S. Reddy, R. Srinivas, C. Venugopal and T. Ramalingam, *Synthesis*, 2001, 1341.

50 K. K. Pasunooti, H. Chai, C. N. Jensen, B. K. Gorityala, S. Wang and X.-W. Liu, *Tetrahedron Lett.*, 2011, **52**, 80.

51 J. Safaei-Ghomi, R. Teymuri and A. Ziarati, *Monatsh. Chem.*, 2013, **144**, 1865.