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Bentonite with high loading of ionic liquid: A potent non-metallic catalyst for the synthesis of dihydropyrimidinones

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ABSTRACT

In attempt to devise an environmentally-benign metal-free catalyst, ionic liquid was supported on bentonite that is a natural clay. To enhance the loading of ionic liquid, bentonite was first functionalized with a dendritic moiety through successive reactions with 2,4,6-trichloro-1,3,5-triazine and 1,3-diaminopropane. Then, the terminal functionalities of dendron were adorned with ionic liquids via reaction with 1-methyl imidazole. The study of the catalytic activity of the resultant catalyst for promoting Biginelli reaction in aqueous media under mild reaction condition approved high activity of the designed composite, superior to that of bentonite. To investigate the role of ionic liquid content in the activity of the catalyst, two model catalysts were prepared through immobilization of ionic liquid on bentonite and bentonite decorated with dendron of lower generation. It was found that the presence of the dendritic moiety could increase grafting of ionic liquid on bentonite and consequently improve the catalytic activity of final catalyst. Notably, the catalyst was highly recyclable. Moreover, analysis of the recycled catalyst indicated the stability of the catalyst.

1. Introduction

Ionic liquid, IL, is referred to a class of salts with low pressure, in which the cationic moiety is organic [1–3]. Considering the diversity of both anions and cations that can be employed for the formation of ILs, numerous ILs with controllable physiochemical properties can be coined [1,4,5]. As ILs benefit from outstanding properties such as low toxicity, high electric conductivity and thermal stability, their uses in various sciences have blossomed rapidly [6–8]. One of the most flourishing utility of ILs is catalysis. In fact, ILs can be utilized as reaction media and catalysts. To improve the catalytic performance of ILs, they are mostly immobilized on supports to furnish heterogeneous catalysts. Taking the increasing importance of green chemistry into account, ILs have been considered as alternatives for metallic catalysts.

Clay materials are extensively utilized in diverse fields, such as catalysis, oil and gas, food, agriculture, ceramics, pharmaceutical and cosmetics. Bentonite, Bent, is one of the most applicable clay that has an aluminum phyllosilicate structure and is of category of silicates with three layers [9–12]. Bent benefits from notable features such as high chemical and thermal stability, good surface area, high adsorption-absorption properties, low-cost and environment benign nature [13–15]. One of the major utility of Bent is supporting the catalytic species. Mostly, supporting materials are surface functionalized prior to the stabilization of the catalysts. Both experimental and computational studies confirmed that ligands with di or multi amino groups are promising functionalization agents [16–21] and can provide effective interactions with the supported catalytic species. In this regard, we have recently studied a library of diamines to disclose the most suitable ligand that can furnish the most efficient interactions with Pd nanoparticles [21]. In some cases, to increase the number of surface functional groups, the supporting materials are first decorated with other organic moieties that possess multiple active sites such as 2,4,6-trichloro-1,3,5-triazine or melamine and then reacted with other heteroatom containing moieties such as diamines, ILs, etc. [4,22,23]. Moreover, introduction of dendritic moieties with multi nitrogen atoms is a promising strategy for surface modification [24–28]. As an example, it was proved that dendrimer decorated halloysite clay is an efficient support for Pd immobilization [28]. This method provides multiple functional groups on the supporting materials.

Biginelli reaction is a well-established multicomponent one-pot reaction that has been widely used for the synthesis of 4-aryl-3,4-dihydropyrimidin-2(1*H*)-one derivatives (DHPMs) [29–34]. As DHPMs are key biologically active chemicals with extensive pharmacological properties [35–38], development of efficient protocols for promoting Biginelli reaction is of great importance. In this regard, disclosing efficient catalysts has been targeted.

The focus of our research team is on the heterogeneous catalysis [39]. In this regard, we tried to use natural clays as catalyst supports [39]. On the other hand, we are interested in developing IL containing catalytic systems for promoting various chemical transformations [8,40]. Recently, we have reported efficient catalysts based on natural

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clay supported ILs [41]. In this topic, one of the challenging issue was low loading of IL on the clay. In attempt to load high content of IL on the clay, in this article Bent clay was selected as a natural support and then adorned with a dendritic moiety, prepared through reaction of 2,4,6-trichloro-1,3,5-triazine and 1,3-diaminopropane. Subsequently, the periphery of the formed dendritic moiety was functionalized with ILs. The resultant composite, Bent-D-IL, was then applied as a metal-free catalyst for promoting Biginelli reaction in aqueous media under mild reaction condition. Investigation of the effective parameters on the reaction, study of the substrate scope and recyclability of the catalyst were also performed.

2. Materials and apparatus

2.1. Materials

The chemicals that have been applied for the synthesis of the catalyst included, 2,4,6-trichloro-1,3,5-triazine (TCT), 3-aminopropyltriethoxysilane (APTES), 1,3-diaminopropane (DAP), 1-methylimidazol, tetrahydrofuran (THF), toluene and MeOH. Biginelli reaction was performed by employing the following reagents: benzaldehydes, ethyl acetoacetate, urea, EtOH and distilled water. All the chemicals and solvents used for the catalyst preparation and Biginelli reaction were provided from Sigma-Aldrich and used without further purification. The applied Bent was purchased from Madan Kavan Co., Iran and used as received.

2.2. Instrumentation and analysis

Formation of Bent-D-IL was verified by analyzing the catalyst by XRD, BET, TGA, FTIR, FE-SEM, EDS and elemental mapping analysis. X-ray diffraction (XRD) pattern of Bent-D-IL was collected on Siemens, D5000 apparatus using graphite monochromatic Cu-Kα. Field emission scanning electron microscope (FE-SEM) images and energy dispersive spectroscopy (EDS) were obtained by MIRA 3 TESCAN-XMU. Fourier transform infrared (FT-IR) spectra were recorded via PERKIN-ELMER-Spectrum 65. Thermo gravimetric analysis (TGA) was accomplished by a METTLER TOLEDO under N_2 atmosphere at heating rate of10 °C min^{-1}.

2.3. Synthesis of the catalyst

2.3.1. Amino-functionalization of Bent: synthesis of Bent-N

In the first step, Bent was functionalized with APTES. In this regard, Bent (3 g) was dispersed in dry toluene and ultrasounded for 10 min. Afterwards, APTES (3 mL) was gradually mixed with the aforementioned suspension. To allow successful functionalization, the mixture was refluxed under N_2 atmosphere at 110 °C overnight. At the end, the precipitate was collected via conventional filtration, washed with toluene repeatedly, and dried in oven at 70 °C.

2.3.2. Introduction of IL-terminated dendritic moiety on Bent-N: synthesis of Bent-D-IL

In order to adorn Bent-N with IL-terminated dendritic moiety, a well dispersed suspension of Bent-N (2 g) in THF (60 mL) was prepared using ultrasonic irradiation. Then, TCT (2 g) was separately dissolved in THF and the resultant solution was slowly added to the Bent-N suspension at 0 °C. To allow the amino functionalities on Bent to react with Cl-functionalities of TCT, the reaction mixture was stirred for 24 h. At the end of the reaction, the precipitate, Bent-TCT, was filtered and after washing with THF dried in oven at 70 °C. In the next step, a suspension of Bent-TCT (1.5 g) in THF (40 mL) was prepared and then reacted with DAP (1.5 g). The reaction was completed after stirring for 24 h at 60 °C to furnish Bent-DAP. The latter was filtered, washed and dried in oven at 80 °C and subsequently treated with TCT using similar procedure explained for the formation of Bent-TCT to furnish Bent-D.

In the final step, to embellish the amino terminal groups of the dendritic moiety with ILs, suspension of Bent-D (1 g) in THF (50 mL) was treated with 1-methylimidazole (1.5 g) under continuous stirring at 65 °C for 24 h under inert atmosphere. Upon completion of the reaction, Bent-D-IL was gathered, washed with MeOH and dried in vacuum oven. The schematic illustration of the synthesis steps for fabrication of Bent-D-IL is depicted in Fig. 1.

2.4. General procedure for the synthesis of dihydropyrimidinones

In a particular procedure, all of the reagents, i.e. benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol) were dissolved in EtOH/H_2O (1:1, 10 mL). Then, Bent-D-IL (50 mg) was introduced and the reaction mixture was stirred at 50 °C. Using TLC technique, the reaction was monitored and after completion, the reaction mixture was diluted with EtOH to dissolve DHPM. Then, Bent-D-IL was simply filtered, washed with EtOH several times and dried in oven overnight. On the other hand, the solvent in the reaction vessel was evaporated and the solid organic product was washed with distilled water to remove the unreacted urea. Further purification was accomplished with column chromatography, using ethyl acetate/hexane mixture.

3. Result and discussion

3.1. Verification of Bent-D-IL formation

FTIR spectroscopy was carried out after each synthetic step. In Fig. 2 the recorded FTIR spectra of Bent, Bent-N, Bent-TCT, Bent-DAP and Bent-D-IL are presented. According to the literature, the bands in the range of 3631–3425 cm^{-1} in the FTIR spectrum of Bent are ascribed to the hydroxyl groups [42–44]. The band at 795 cm^{-1} is assigned to the typical stretching modes of Si—O for silica, while the bands at 1032 cm^{-1} and 526 cm^{-1} are related to the absorption band of Si—O—Si and Al—O—Si deformation respectively. Moreover, the band at 1636 cm^{-1} is attributed to the stretching vibration of water molecules [42–44]. In the FTIR spectrum of Bnet-N, similar characteristic bands are discerned, indicating that reaction with APTES did not lead to the collapse of Bent structure. Notably, the observed band at 2927 cm^{-1} is assigned to –CH_2 functionality in APTES. Other characteristic bands of APTES, i.e. Si—O—Si and Si—O stretching, overlapped with the bands of Bent. Similarly, for three other samples, Bent-TCT, Bent-DAP and Bent-D-IL, the characteristic bands of Bent are discerned. This observation confirms the stability of Bent structure upon decoration with IL-terminated dendritic moiety. The distinguishing point in the FTIR spectra of the mentioned spectra is the appearance of an additional band at 1720 cm^{-1} that is corresponded to the —C═N functionality in the TCT and IL structure. In fact, this characteristic band can demonstrate conjugation of D-IL.

Next, the XRD pattern of Bent-D-IL was obtained to appraise whether incorporation of IL terminated dendritic moiety can affect the structure of Bent. As illustrated in Fig. 3, in the recorded XRD pattern of Bent-D-IL the characteristic bands of Bent at $2\theta = 7°$, 20.8°, 21.9°, 26.6°, 27.7°, 31.7°, 36°, 50°, 62°, 73.5° and 76° can be discerned [45,46]. This result corroborated that functionalization of Bent with D-IL did not alter Bent structure.

Using SEM technique, the morphologies of both Bent and Bent-D-IL were analyzed (Fig. 4). As depicted, Bent exhibited a flake-like morphology, while Bent-D-IL showed a distinguished morphology from Bent. The change of morphology upon introduction of IL-containing functionality is quite expectable. In fact, the non-covalent interactions of IL moieties of the backbone of Bent-D-IL could affect the morphology. To further approve conjugation of the organic moiety on the clay, EDS analysis was exploited. As shown, in EDS analysis of Bent, Al, Ca, K, Cu, Mg, Fe, O and Si atoms can be observed. In the EDS analysis of Bent-D-IL, these atoms can also be discerned. Additionally, C, N and Cl atoms can be observed in the EDS analysis of the catalyst, indicating conjugation

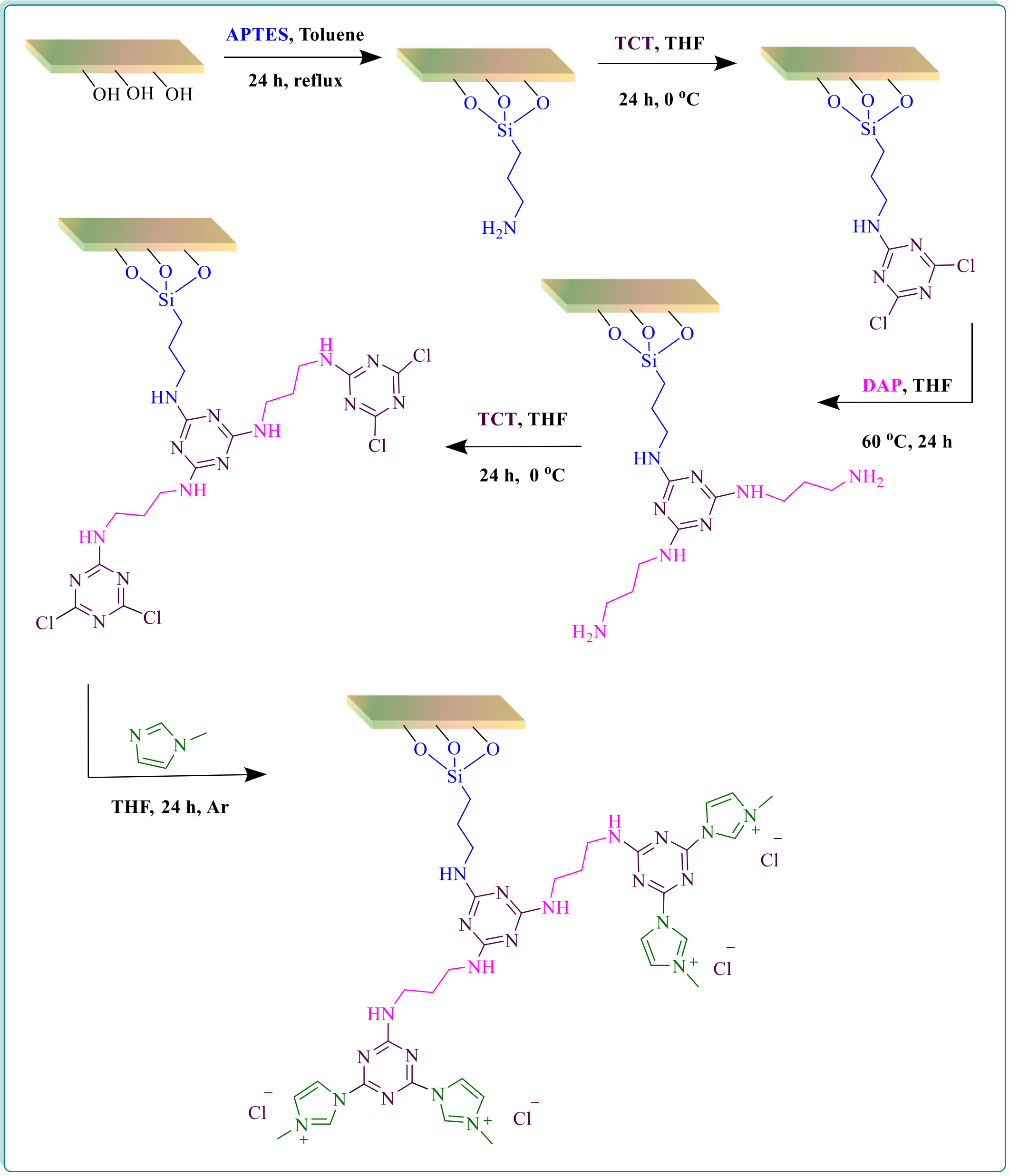


Fig. 1. Synthetic procedure of Bent-D-IL.

of the organic functionality (D-IL) on the backbone of the catalyst. Notably, some of the Cl functionalities on TCT can not find an opportunity to participate in the reaction with diamine due to the steric effect. This issue is in good accordance with the literature [47].

Elemental mapping analysis of the Bent-D-IL (Fig. 5) was also carried out to disclose the dispersion of the organic functionality on Bent. As illustrated, C, N and Cl atoms showed high dispersion, implying that IL-containing dendritic moiety was grafted on Bent almost uniformly.

A potent analysis that can approve grafting of the organic functionalities is TG analysis. In this regard, TG curves of Bent-N, Bent-TCT, Bent-DAP and Bent-DIL were obtained and compared, Fig. 6. The comparison of all four curves implied that the thermal stability of the samples decreased as Bent-N > Bent-TCT > Bent-DAP > Bent-D-IL. This is a logical result, as by addition of more organic moieties, it is expected that the thermal stability decreases. In fact, the degradation of the organic functionalities can justify the observed decrement of the thermal stability. In more detail, in Bent-N, apart from weight loss due to loss of water, one weight loss step is observed at 280 °C (~1.5 wt%) that is corresponded to the decomposition of APTES and another weight loss is appeared in the range of 450–560 °C that is related to the decomposition of Bent. Similarly, in TG curve of Bent-TCT, weight losses due to the loss of water and decomposition of Bent are observed. Moreover, the weight loss appeared in the range of 300–370 °C (6 wt%) confirmed conjugation of TCT. Thermogram of Bent-DAP was similar to that of Bent-TCT, except, the weight loss in the range of 280–350 °C was ~8.8 wt%, approving grafting of DAP. In TG curve of Bent-D-IL, apart from loss of structure of water and Bent decomposition, a weight loss was observed in the range of 240–350 °C (11.7 wt%). These results established successful grafting of organic moieties in each synthetic step.

In the following, both Bent and Bent-D-IL were analyzed by BET technique, Fig. 7. The results signified that the specific surface area of the used Bent was 40.62 $m^2 g^{-1}$. This value for Bent-D-IL dramatically reduced and reached to 5.19 $m^2 g^{-1}$, approving grafting of IL-terminated dendritic moiety.

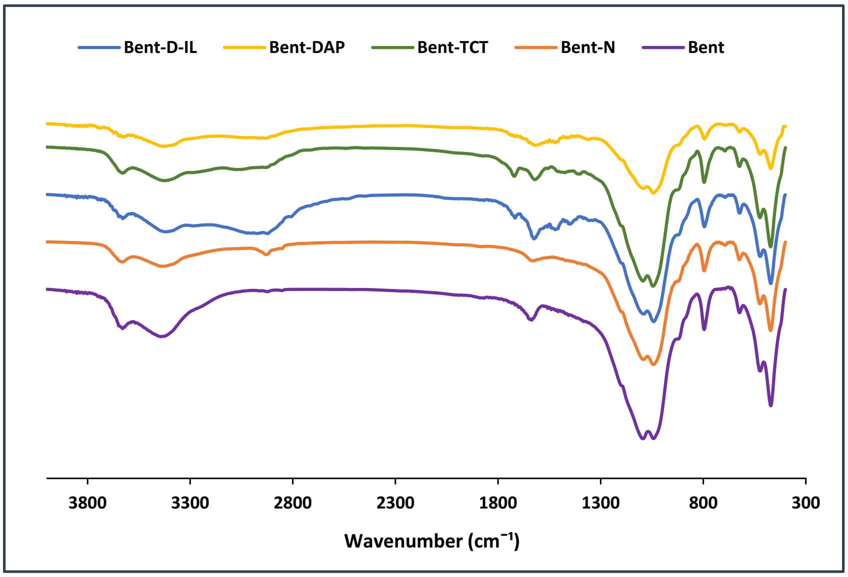


Fig. 2. FTIR spectra of Bent, Bent-N, Bent-TCT, Bent-DAP and Bent-D-IL.

3.2. Catalyst activity

In this article, it was intended to design a heterogeneous metal-free catalyst by supporting ILs on a low-cost and readily available clay, Bent. According to our experiences on functionalization of clays and other reports, direct grafting of ILs on clay surface resulted in low loading of IL [41]. To cope with this challenging issue, a dendritic moiety that contained several reactive sites for conjugation of IL was first grown on Bent and then, IL was introduced. After confirmation of the formation of Bent-D-IL, its activity was assessed. In this regard, one of the most conventional chemical transformation, Biginelli reaction, was selected. The importance of this reaction is formation DHPMs that are precious heterocycles with potential biological activities. To commence the study, a model reaction, reaction of benzaldehyde, ethyl acetoacetate and urea, was targeted. First, to elucidate the necessity of the presence of the catalyst for this reaction, the model reaction was performed in the absence of the catalyst at 50 °C in H_2O/EtOH (1:1). The results, Table 1, approved that in the absence of the catalyst only low yield of the desired product was furnished (10%). This result emphasized the necessity of use of the catalyst for this reaction.

Confirming the importance of the use of the catalyst, the reaction condition was optimized. First, the model reaction was performed by loading 30 mg Bent-D-IL in water at 50 °C, Table 1. Under this condition, low yield of the product was obtained after relatively long reaction time. To increase the reaction yield, the reaction solvent was changed to H_2O/EtOH (1:1). The result indicated significant improvement of the reaction yield. Taking the important effect of solvent into account, the effects of other solvents were also investigated. The results implied that H_2O/EtOH (1:1) led to the best results. Next, the loading of the catalyst was optimized. As shown, increment of the catalyst loading to 50 mg effectively improved the yield of the reaction. Hence, for further investigation, this value was considered as the optimum catalyst loading. Reaction temperature effect was also appraised. To this purpose, the reaction was performed at two additional temperatures, 25 and 60 °C. The

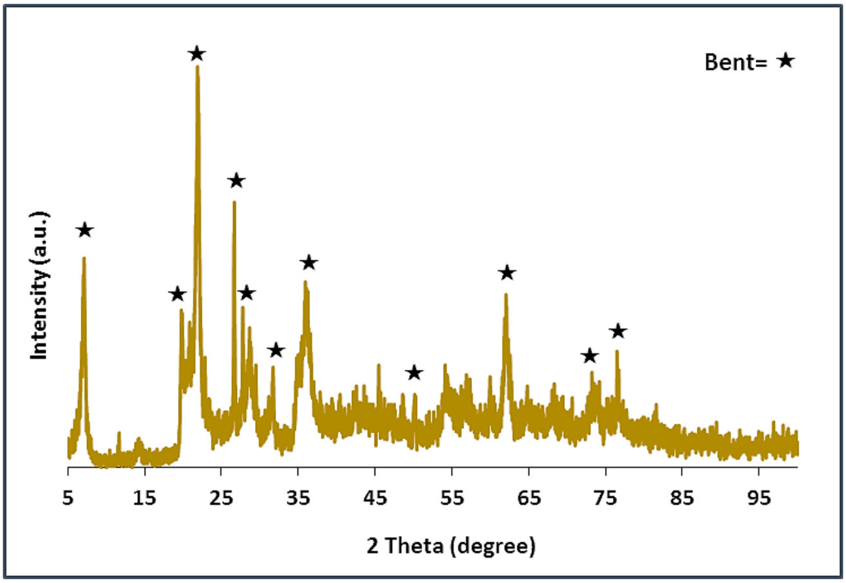


Fig. 3. XRD pattern of Bent-D-IL.

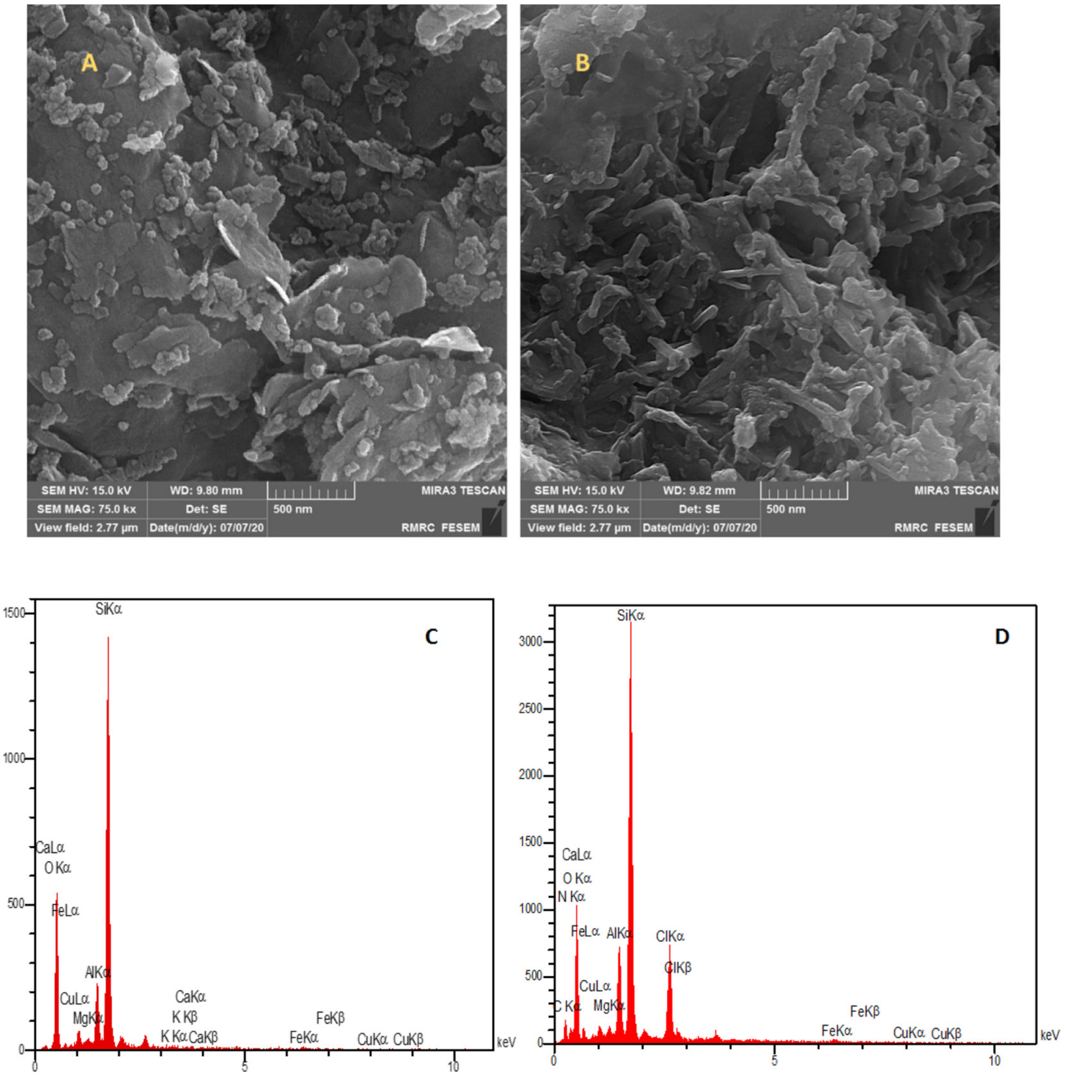


Fig. 4. A) FESEM image of Bent, B: SEM image of Bent-D-IL, C and D) EDS analyses of Bent and Bent-D-IL.

results implied that at lower temperature, the reaction yield decreased, while increment of the temperature from 50 to 60 °C had no effect on the reaction yield. Hence, the best temperature was selected as 50 °C.

3.3. Investigation of roles of IL and Bent in the catalysis

High catalytic activity of Bent-D-IL motivated us to study the roles of Bent and IL in catalysis more precisely. To fulfill this issue, it was first examined whether bare Bent has any catalytic activity. In this regard, the model Biginelli reaction was performed in the presence of Bent as a catalyst under the optimum reaction condition. It was found that only low yield of the desired product (25%) was furnished by using Bent as a catalyst. This result confirmed that IL is the main catalytic species and its presence is essential for obtaining high yield of the reaction.

3.4. Study of the role of IL content in the catalysis

Confirming the main role of IL in the catalysis, it was appraised whether the content of IL on the structure of Bent-D-IL can affect the catalytic activity. In this regard, some model catalysts with different loading of ILs were prepared and their activities for the model Biginelli reaction were compared. One of the control catalyst, denoted as Bent-IL, was prepared through —Cl functionalization of Bent (the procedure was similar to that used for the synthesis of Bent-N, except instead of APTES, (3-chloropropyl)triethoxysilane was applied), followed by reaction with 1-methylimidazol. The second control catalyst, referred as Bent-TCT-IL, was fabricated through reaction of Bent-TCT with 1-methylimidazol. The results of the comparison of the activities of these two control catalysts with that of the catalyst, Table 2, indicated that the content of IL in the structure of the catalyst significantly affected the activity of the catalyst and higher content of IL resulted in superior catalytic activity. Another point that can be inferred from the tabulated results is that the content of IL on the structure of the catalyst is influenced by the presence of the dendritic moiety. In more detail, in Bent-IL, the loading of IL is very low. This observation is expectable because TG analysis confirmed that loading of (3-chloropropyl)triethoxysilane on Bent was very low (~1 wt%). Hence, just a few molecules of 1-methylimidazol have the chance of grafting on Bent. The TG analysis of Bent-TCT-IL showed that introduction of TCT prior to conjugation of IL led to the increase of IL content. This is a rational result as each attached TCT molecule on Bent can provide two opportunities for IL grafting. Comparing the IL content of Bent-IL and Bent-TCT-IL, it can be seen that the loading of IL in the latter is slightly lower than two fold. This can be due to the fact that some of Cl functionalities on Bent-TCT had no chance to react with 1-methylimidazol as a result of steric hindrance. Similarly, in Bent-D-IL sample, IL content increased by introduction of another generation of dendritic moiety and more possible grafting sites. These results corroborated that introduction of

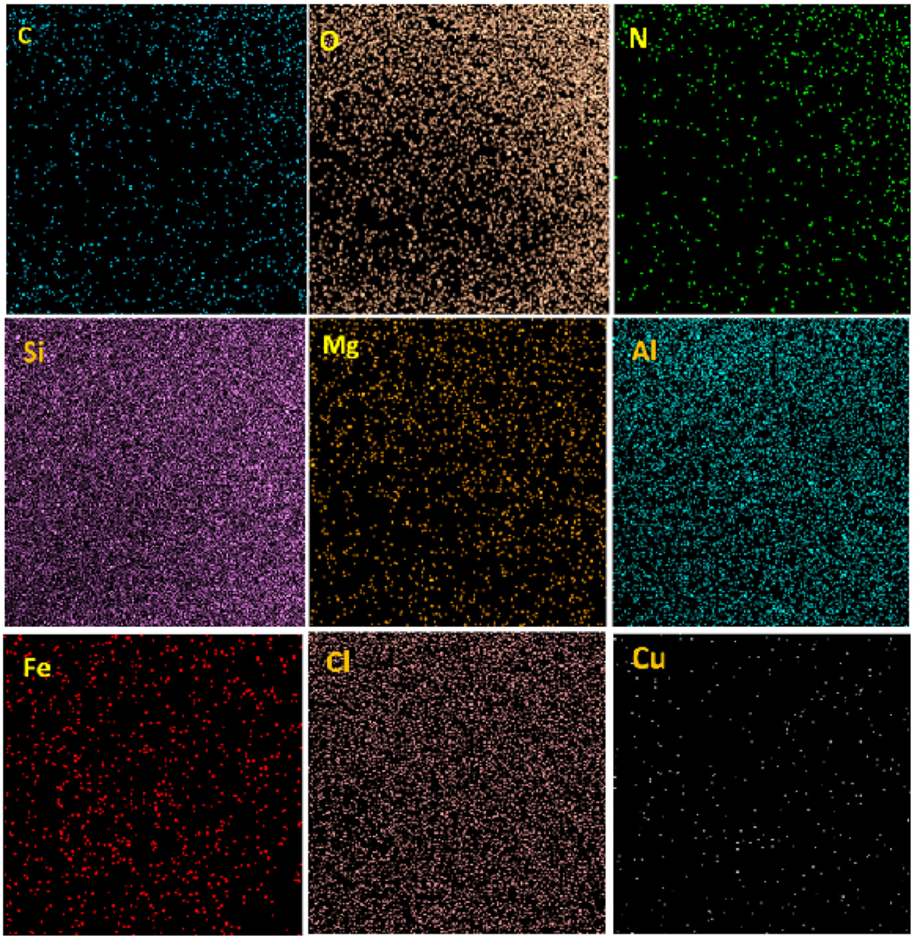


Fig. 5. Elemental mapping analysis of Bent-D-IL.

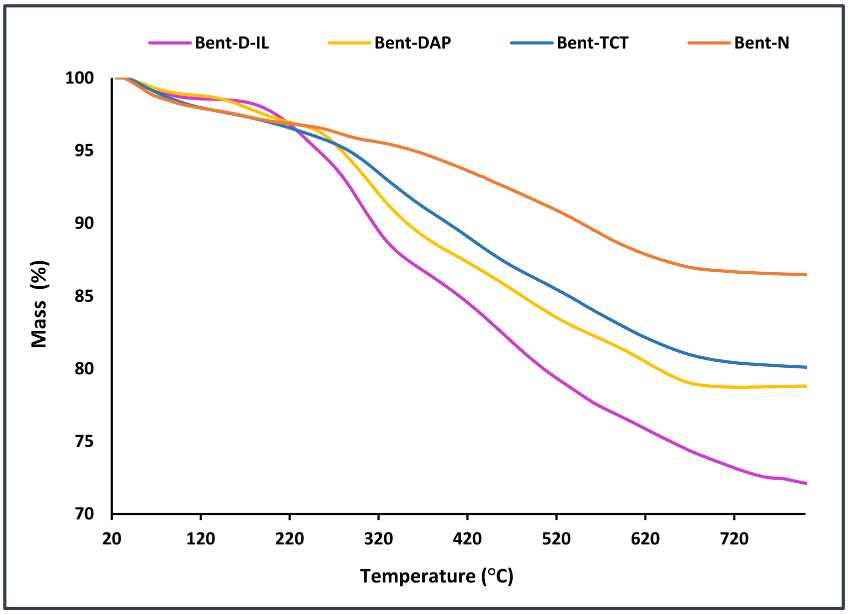


Fig. 6. Thermograms of Bent-N, Bent-TCT, Bent-DAP and Bent-D-IL.

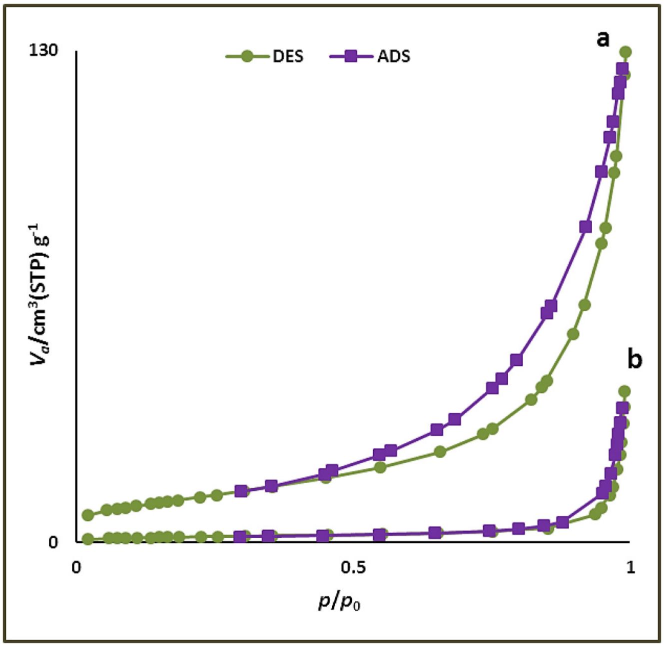


Fig. 7. N_2-adsorption desorption isotherm of the a) Bent and b) Bent-D-IL.

a dendritic moiety is an efficient strategy to improve loading of IL on Bent clay.

3.5. Generality of the present protocol

Next, it was appraised whether the observed results for the model reagents can be generalized to other substrates. In this regard, the reactions of a variety of aromatic aldehydes with electron-donating and electron-withdrawing functionalities were performed under Bent-D-IL catalysis. Gratifyingly, aromatic aldehydes with different electronic densities could tolerate Biginelli reaction to give raise to the corresponding DHPMs, Table 3. Noteworthy, even the heterocyclic aldehyde could undergo the reaction to furnish the product in high yield.

3.6. Comparison of the catalytic activity

As mentioned, Biginelli reaction is an important organic reaction that has been focus of many researchers and till now many protocols have been developed to furnishe DHPMs efficiently. Although exact comparison of the reported methods is not possible, in this section, some reported reaction conditions and yields of the model DHPMs are tabulated in Table 4 to disclose whether the present protocol by using Bent-D-IL can be placed among the efficient methodologies. The results summarized in Table 4 indicated that both metallic and metal free catalysts have been utilized for catalyzing Biginelli reaction. On the other hand, use of clays and ILs has also been considered. Considering the economic and environmental issues, applications of natural compounds as catalysts or catalyst supports is of great interest. In fact, although synthetic supports such as MCM-41 benefit from some advantageous such as tunable properties, their syntheses are mostly carried out in several steps that rendered them time consuming, tedious and expensive. On the other hand, metal free catalysts and use of aqueous media as reaction media are in agreement with the principles of Green chemistry. Considering the fact that the yield of all tabulated protocols are almost comparable, it can be inferred that Bent-D-IL that is a metal free catalyst is an efficient catalyst that can promote Biginelli reaction in aqueous media to furnish the corresponding products in high yields.

Table 2
Study of the effect of IL content on the catalytic activity.

Entry	Catalyst	IL content (wt%)	Yield[a] (%)
1	Bent-IL	1	68
2	Bent-TCT-IL	1.8	78
3	Bent-D-IL	3	98

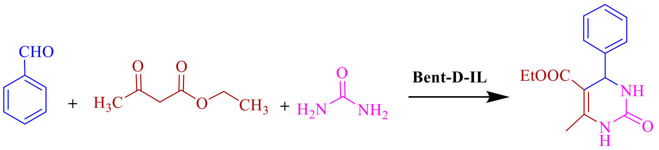
[a] Reaction condition: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), catalyst (50 mg), H_2O/EtOH (10 mL) at 50 °C in 3 h.

3.7. Catalyst recyclability

To evaluate the recyclability of Bent-D-IL, the catalyst was recovered from first run of Biginelli model reaction and then utilized for the next run of the same reaction. Measurement of the yield of the reaction established that use of Bent-D-IL for the second run of Biginelli model reaction caused no decrement of the catalytic activity and the corresponding DHPMs derivative was formed in high yield. Recovery and use of the catalyst for the third run, however, resulted in slight decrease of the initial activity. This trend continued and the yield of the reaction decreased from 100 to 82% after using Ben-D-IL for five runs. Notably, after sixth run, 7% loss of the activity was observed, Fig. 8.

To shed light to the impact of reusing Bent-D-IL on the morphology, the reused catalyst after sixth run was characterized by SEM. As

Table 1
Optimization of Biginelli reaction condition.

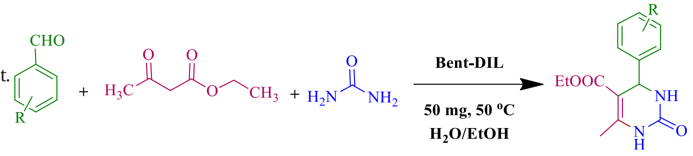


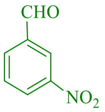
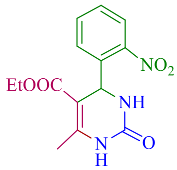
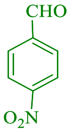
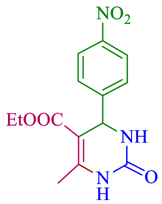
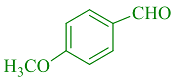
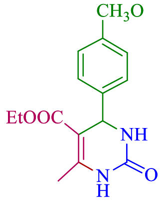
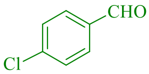
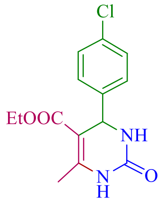
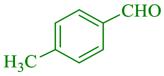
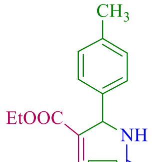
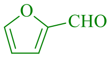
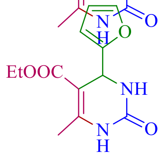
Entry	Catalyst (mg)	Temp. (°C)	Solvent[a]	Time (h:min)	Yield[b] (%)
1	30	50	H_2O	5:30	20
2	30	50	H_2O/EtOH	4:00	60
3	30	50	CH_3CN	4:00	40
4	30	50	DMF	5:00	20
5	30	50	THF	5:00	30
6	40	50	H_2O/EtOH	4:00	85
7	50	50	H_2O/EtOH	3:00	98
8	50	60	H_2O/EtOH	2:40	98
9	50	25	H_2O/EtOH	4:00	65
10	–	50	H_2O/EtOH	6:00	10

[a] Reaction condition: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol).
[b] Isolated yields.

Table 3

Synthesis of DHPMs by using Bent-D-IL as the catalyst.



No.	Substrate	Product[a]	Yield[b] (%)
1			98
2			100
3			90
4			95
5			90
6			85

[a] Reaction condition: aldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), catalyst (50 mg), H_2O/EtOH (10 mL) at 50 °C in 3 h.
[b] Isolated yield.

illustrates in Fig. 8, the reused catalyst exhibited more aggregated morphology compared to fresh Bent-D-IL. FTIR spectrum of reused Bent-D-IL after sixth run was also obtained and compared with that of fresh Bent-D-IL. As shown, FTIR spectrum of the reused catalyst exhibits all of the characteristic absorbance bands of fresh Bent-D-IL, approving the stability of Bent-D-IL in the course of reusing.

4. Conclusion

In summary, a novel heterogeneous catalyst was devised by adorning Bent with a dendritic moiety and introduction of ILs. In this regard, bentonite was first functionalized with a dendritic moiety through successive reactions with TCT and 1,3-diaminopropane. Then, the terminal functionalities of dendron were adorned with ILs via reaction with 1-methyl imidazole. Notably, some of the Cl functionalities on TCT can not find an opportunity to participate in the reaction with diamine due to the steric effect. The resulting catalyst, Bent-D-IL, exhibited high catalytic activity for catalyzing Biginelli reaction in aqueous media under mild reaction condition. This protocol can be generalized to various substrates for the formation of broad range of DHPMs in high yields. Investigation of the role of the dendritic moiety in the increase of IL content on the structure of the catalyst indicated that the dendritic moiety could effectively improve IL loading and consequently the observed catalytic activity. It is worth mentioning that the catalyst was recyclable up to six runs and analysis of the recycled catalyst indicated the stability of catalyst.

Table 4

Comparison of the catalytic activity of the present catalyst with other reported catalysts for Biginelli reaction.

Entry	Catalyst	Catalyst amount	Condition	Solvent	Time (h:min)	Yield (%)	Ref
1[a]	PANI-$FeCl_3$	0.2 g	Reflux	CH_3CN	24:00	83	[48]
2[b]	HBF_4	10 mol%	45 °C	Solvent-free	00:35	95	[49]
3[c]	AT-Mont	0.02 g	Reflux	EtOH	2:00	98	[50]
4[d]	(0.5)$ILHSO_4$@MCM-41@Cu(15)	0.5 g	80 °C	EtOH	2:00	90	[51]
5[e]	30% TPA/bent	0.09 g	80 °C	EtOH	5:00	95	[52]
6	Silica sulfuric acid	0.23 g	Reflux	EtOH	6:00	91	[53]
7[f]	Fe(III)/Al-MCM-41	0.03 g	Reflux	CH_3CN	4:00	85	[54]
8[g]	β-CD-SO_3H	0.04 g	100 °C	Solvent-free	2:00	89	[55]
9	Bent-DIL	0.05 g	50 °C	H_2O/EtOH	3:00	95	This study

[a] Polyaniline supported $FeCl_3$.

[b] Fluoroboric acid.

[c] Acid activated montmorillonite clay.

[d] Copper-doped mesoporous silica supported dual acidic ionic liquid.

[e] Heteropolyacid 12-tungstophosphoric acid $H_3[PW_{12}O_{40}]$ immobilized over natural bentonite.

[f] $FeCl_3$ immobilized on Al-MCM-41.

[g] β-Cyclodextrin–SO_3H.

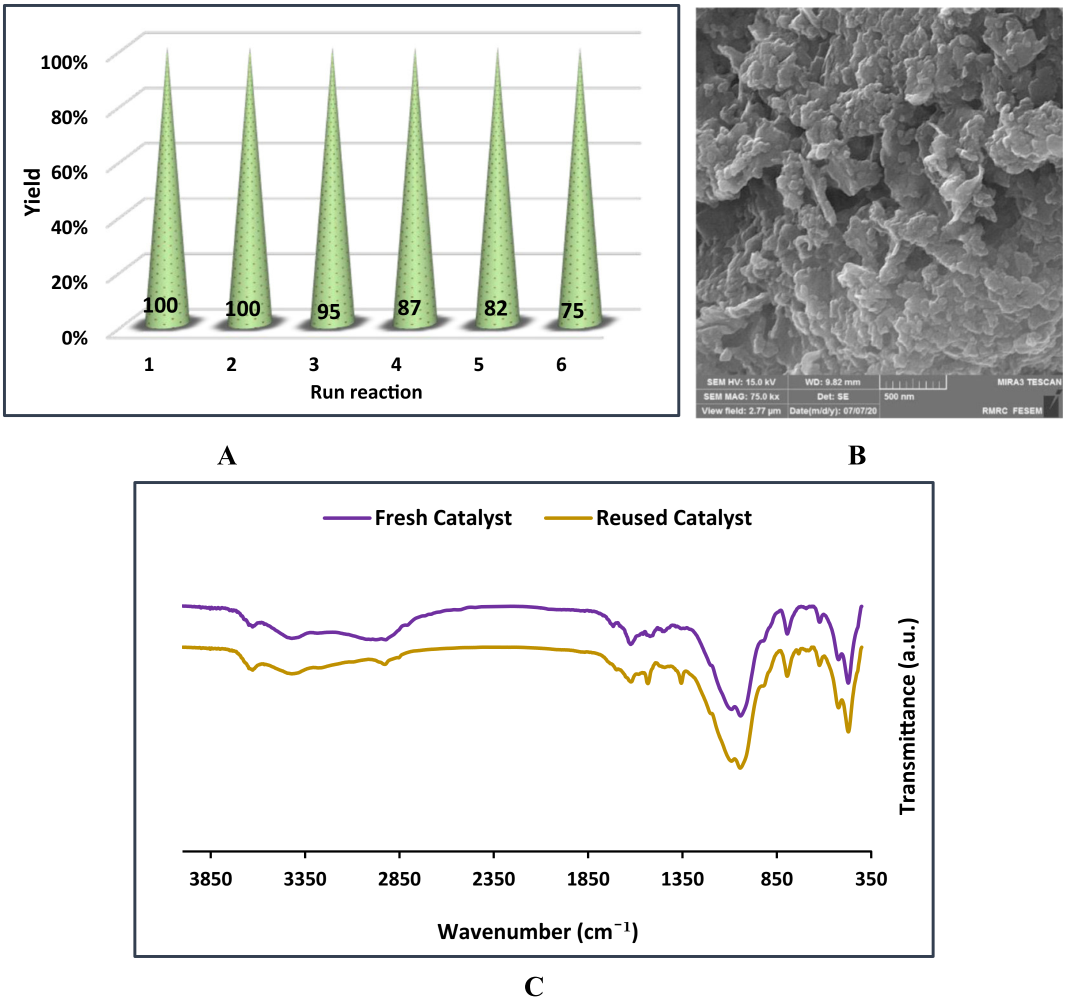


Fig. 8. A: The results of the recyclability of Bent-DIL and B: SEM image and C: FTIR spectrum of the recycled catalyst.

CRediT authorship contribution statement

Samahe Sadjadi: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision. **Fatemeh Koohestani:** Formal analysis, Methodology, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] F. Karimi, M.A. Zolfigol, M. Yarie, Mol. Catal. 463 (2019) 20.
[2] R. Teimuri-Mofrad, M. Gholamhosseini-Nazari, E. Payami, S. Esmati, Appl. Organomet. Chem. 32 (2018), e3955.
[3] E. Rafiee, M. Kahrizi, J. Mol. Liq. 218 (2016) 625.
[4] S. Sadjadi, M.M. Heravi, B. Masoumi, S.S. Kazemi, J. Coord. Chem. 72 (2019) 119.
[5] B.Ö. Öztürk, Microporous Mesoporous Mater. 267 (2018) 249.
[6] S. Sadjadi, M.M. Heravi, M. Malmir, F.G. Kahangi, Appl. Clay Sci. 162 (2018) 192.
[7] S. Sadjadi, M.M. Heravi, M. Raja, Carbohydr. Polym. 185 (2018) 48.
[8] S. Sadjadi, F. Koohestani, Int. J. Biol. Macromol. 147 (2020) 399.
[9] H. Faghihian, M.H. Mohammadi, Appl. Surf. Sci. 264 (2013) 492.
[10] J. Amaya, L. Bobadilla, L. Azancot, M. Centeno, S. Moreno, R. Molina, Mater. Res. Bull. 123 (2020) 110728.
[11] D. Wan, G. Wang, W. Li, X. Wei, Appl. Surf. Sci. 413 (2017) 398.
[12] M. Nasrollahzadeh, S.M. Sajadi, M. Maham, J. Mol. Catal. A Chem. 396 (2015) 297.
[13] A. Rostami-Vartooni, L. Rostami, M. Bagherzadeh, J. Mater. Sci. Mater. Electron. 30 (2019), 21377.
[14] M. Nasrollahzadeh, S.M. Sajadi, M. Maham, I. Kohsari, Micropor. Mesopor. Mat 271 (2018) 128.
[15] Z. Li, Y. Sun, Y. Yang, Y. Han, T. Wang, J. Chen, D.C. Tsang, Environ. Res. 183 (2020) 109156.
[16] H. Alamgholiloo, S. Rostamnia, A. Hassankhani, X. Liu, A. Eftekhari, A. Hasanzadeh, K. Zhang, H. Karimi-Maleh, S. Khaksar, R.S. Varma, M. Shokouhimehr, J. Colloid Interface Sci. 567 (2020) 126.
[17] S. Sadjadi, F. Koohestani, N. Bahri-Laleh, Appl. Clay Sci. 192 (2020) 105645.
[18] A. Savari, F. Heidarizadeh, N. Pourreza, Polyhedron 166 (2019) 233.
[19] N. Sahiner, S.B. Sengel, Appl. Clay Sci. 146 (2017) 517.
[20] S. Dehghani, S. Sadjadi, N. Bahri-Laleh, M. Nekoomanesh-Haghighi, A. Poater, Appl. Organomet. Chem. 33 (2019), e4891.
[21] M. Tabrizi, S. Sadjadi, G. Pareras, M. Nekoomanesh-Haghighi, N. Bahri-Laleh, A. Poater, J. Colloid Interface Sci. 581 (2021) 939–953.
[22] S. Sadjadi, P. Mohammadi, M. Heravi, Sci. Rep. 10 (2020) 6535.
[23] M. Bahadori, S. Tangestaninejad, M. Moghadam, V. Mirkhani, A. Mechler, I. Mohammadpoor-Baltork, F. Zadehahmadi, Microporous Mesoporous Mater. 253 (2017) 102.
[24] Y. Jing, L. Wei, Y. Wang, Y. Yu, Micropor. Mesopor. Mat 183 (2014) 124.
[25] E.J. Acosta, C.S. Carr, E.E. Simanek, D.F. Shantz, Adv. Mater. 16 (2004) 985.
[26] M. Tarahomi, H. Alinezhad, B. Maleki, Appl. Organomet. Chem. 33 (2019), e5203.
[27] S. Lai, J. Gao, H. Zhang, L. Cheng, X. Xiong, J. CO$_2$ Util. 38 (2020) 148.
[28] N. Bahri-Laleh, S. Sadjadi, A. Poater, J. Colloid Interface Sci. 531 (2018) 421.
[29] A.M. Shumaila, A.A. Al-Thulaia, Synth. Commun. 49 (2019) 1613.
[30] L.V. Chopda, P.N. Dave, ChemistrySelect 5 (2020) 5552.
[31] D. Shobha, M. Chari, A. Mano, S. Selvan, K. Mukkanti, A. Vinu, Tetrahedron 65 (2009), 10608.
[32] A. Khazaei, M.A. Zolfigol, S. Alaie, S. Baghery, B. Kaboudin, Y. Bayat, A. Asgari, RSC Adv. 6 (2016) 10114.
[33] M. Nasr-Esfahani, M. Taei, RSC Adv. 5 (2015) 44978.
[34] S. Rostamnia, A. Morsali, RSC Adv. 4 (2014) 10514.
[35] P. Slobbe, E. Ruijter, R.V. Orru, MedChemComm 3 (2012) 1189.
[36] S.R. Jetti, A. Upadhyaya, S. Jain, Med. Chem. Res. 23 (2014) 4356.
[37] K.S. Atwal, B.N. Swanson, S.E. Unger, D.M. Floyd, S. Moreland, A. Hedberg, B.C. O'Reilly, J. Med. Chem. 34 (1991) 806.
[38] D. Russowsky, R.m.F. Canto, S.A. Sanches, M.G. D'Oca, Â. de Fátima, R.A. Pilli, L.K. Kohn, M.A. Antoˆnio, J.E. de Carvalho, Bioorg. Chem. 34 (2006) 173.
[39] S. Sadjadi, Appl. Clay Sci. 189 (2020) 105537.
[40] S. Sadjadi, F. Koohestani, J. Mol. Liq. 301 (2020) 112414.
[41] S. Sadjadi, M.M. Heravi, M. Malmir, B. Masoumi, Appl. Organomet. Chem.
[42] B. Bananezhad, M.R. Islami, E. Ghonchepour, H. Mostafavi, A.M. Tikdari, H.R. Rafiei, Polyhedron 162 (2019) 192.
[43] A. Szymaszek, M. Kubeł, B. Samojeden, M. Motak, Chem. Eng. Process. (2020) 13.
[44] Q.U. Ain, H. Zhang, M. Yaseen, U. Rasheed, K. Liu, S. Subhan, Z. Tong, J. Clean. Prod. 247 (2020) 119088.
[45] M. Naswir, S. Arita, S. Marsi, J. Clean Energy 1 (2013).
[46] M. Niu, G. Li, L. Cao, X. Wang, W. Wang, J. Clean. Prod. (2020) 120700.
[47] S. Sadjadi, F. Ghoreyshi Kahangi, M. Dorraj, M.M. Heravi, Molecules 25 (2020) 241.
[48] H.A. Patel, A.M. Sawant, V.J. Rao, A.L. Patel, A.V. Bedekar, Catal. Lett. 147 (2017) 2306.
[49] W. Chen, S. Qin, J. Jin, Catal. Commun. 8 (2007) 123.
[50] A. Phukan, S.J. Borah, P. Bordoloi, K. Sharma, B.J. Borah, P.P. Sarmah, D.K. Dutta, Adv. Powder Technol. 28 (2017) 1585.
[51] N. Yao, M. Lu, X.B. Liu, J. Tan, Y.L. Hu, J. Mol. Liq. 262 (2018) 328.
[52] L.V. Chopda, P.N. Dave, Arab. J. Chem. 13 (2020) 5911–5921.
[53] P. Salehi, M. Dabiri, M.A. Zolfigol, M.A.B. Fard, Tetrahedron Lett. 44 (2003) 2889.
[54] H.A. Oskooie, M.M. Heravi, N. Karimi, M.H. Monjezy, Synth. Commun. 41 (2011) 826.
[55] S. Asghari, M. Tajbakhsh, B.J. Kenari, S. Khaksar, Chin. Chem. Lett. 22 (2011) 127.