

# Studies on Structural Changes and Catalytic Activity of Y-zeolite Composites of 1,3-disulfoimidazolium trifluoroacetate Ionic Liquid (IL) for Three Component Synthesis of 3,4-dihydropyrimidinones

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Abstract This report describes the development of six acidic composites of Y-zeolite with 1,3-disulfoimidazolium trifluoroacetate [Dsim][CF<sub>3</sub>COO] ionic liquid (IL) and displays the gradual increase of acidic IL mediated dealumination within zeolite framework with increasing loading in Powder XRD and IR studies. The structural changes of modified framework of zeolite were analyzed by SEM-EDX, TEM, TGA, BET and UV–Vis techniques. Out of the six composites, the more acidic [Dsim][CF<sub>3</sub>COO]/ NaY = 20% (e) composite was evaluated as heterogeneous catalyst for multicomponent synthesis of 3,4-dihydropyrimidinones (DHPMs) under neat condition at various temperature.

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# 1 Introduction

**Graphical Abstract** 

The concept of "Supported Ionic Liquid Phase" (SILP) is pervasive and it focuses to transfer the desired properties of ionic liquid (IL) to support substances by confining the fluid to the surface mainly through physisorption and in a few cases by chemisorption. Such immobilization of IL may generate 'designer surfaces' with properties of both components [1–3]. Many applications of SILP have been observed in last decade as functional materials for generation of heterogeneous catalysts, surface modifying agents, stationary phases in separation techniques and in electrochemistry [4–6]. Generally, organic synthesis utilize higher

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amount of IL as recyclable greener medium or catalyst in homogeneous condition with or without any catalyst. The transfer of unique physicochemical properties of IL on solid support combines the advantages of both homogeneous and heterogeneous catalysis, with facile separation from the reaction mixture. Furthermore, based on their capacity to stabilize the catalyst in organic reactions, such heterogenized catalysts include several advantages over free IL such as high thermal and water stability, leaching stability, safe handling and easy recycling through filtration. Thus, they can effectively resolve the difficulties in separation of products, and achieve high recoverability and reusability of catalysts. Studies reveal that the use of immobilized task-specific ILs as catalytic system also modifies the process of catalytic reactions, affecting reaction rate, eliminate undesirable reactions, increase product selectivity and even enantioselective activity of asymmetric reactions [7, 8]. For preparation of functionalized hybrid material of ionic liquids, NaY zeolite is considered as suitable choice for its well organized pore channels, high surface area and thermal stability in addition to environment friendly nature [**9**].

The present work aims to study the immobilization of -SO<sub>3</sub>H functionalized 1,3-disulfoimidazolium trifluoroacetate [Dsim][CF<sub>3</sub>COO] in NaY zeolite with different loading of IL and study their structural changes of basic framework using Powder XRD, FT-IR, SEM-EDX, TEM, TGA, BET and UV-Vis techniques. The acidity of each IL composite is determined from Hammett function and evaluated as heterogeneous catalyst for three-component preparation of Biginelli 3,4-dihydropyrimidinones in solvent-free medium at 60°C and also under solvent-free mechanochemical method at ambient temperature (Scheme 1). 3.4-Dihyropyrimidinones (DHPMs) and their derivatives are well known heterocycles in the realm of natural and synthetic chemistry for its diverse therapeutic and pharmacological properties including antitumor, antiviral, anti-inflammatory and antibacterial activities [10–14]. A large number of traditional Lewis or Brønsted acids catalysts have been reported for the formation of DHPMs with various limitations such as strong acidic condition, high temperature reaction, longer reaction time, use of organic solvent and non-recycling of catalyst [15-17]. To overcome those disadvantages, several modified protocols have been designed in the following years by means of microwave irradiation [18], ultrasound irradiation [19], ionic liquids [20], mechanochemical method [21] and different types of recyclable acidic, nanoparticle, metal oxides such as lanthanide triflate [22], indium(III) halides [23], Sr(OTf)<sub>2</sub> [24], nanomagneticsupported sulfonic acid [25], FeCl<sub>3</sub>-supported nanopore silica [26], nanosilica-supported Sn(II) chloride [27], Fe<sub>3</sub>O<sub>3</sub> [28] and boehmite nanoparticle [29], metal oxide-MWC-NTs [30], and so on. In spite of their prospective efficacy,



Scheme 1 Synthesis of 3,4-dihydropyrimidinone derivatives 4

chemists are still searching for efficient method under mild condition with higher yields.

### 2 Experimental

### 2.1 General Remarks

The chemicals were purchased from different commercial suppliers in pure state. Powder XRD patterns of samples were recorded with a Rigaku (miniflex UK) X-ray diffractometer using Cu Ka radiation (0.15418 nm) operated at 30 kVand 15 mA at a scan speed of  $2^{\circ}$  min<sup>-1</sup> and 2 $\theta$  range of 5-70°. The <sup>1</sup>HNMR and <sup>13</sup>CNMR were recorded in a JEOL 400 MHz spectrometer ( $\delta$  in ppm) in DMSO-d6 solvent. FT-IR spectra were recorded in Perkin-Elmer FT-IR spectrometer. Hammett acidity of ionic liquid composite material was measured in a UV 2550 spectrophotometer. Shimadzu TGA 50 instrument was used for thermogravimetric analysis. All elemental analyses were obtained from Perkin Elmer 20 analyzer. Melting points of DHPMs were recorded on a Buchi-560 apparatus. Nitrogen adsorption-desorption isotherm of IL loaded NaY composites was measured in Quantachrome ASiQWin apparatus. Scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX) analyses were carried out with a JEOL JSM-6390LV SEM equipped with an Energy-Dispersive X-ray analyzer. Transmission electron microscopic (TEM) images were carried out on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV.

# 2.1.1 General Procedure for Preparation of Six Composites of [Dsim][CF<sub>3</sub>COO]/NaY

The synthesis of  $[Dsim][CF_3COO]/NaY$  composite involved in two steps. Initial step utilized for synthesis of 1,3-disulfoimidazolium trifluoroacetate  $[Dsim][CF_3COO]$ IL according to literature procedure [31]. Wet impregnation method was used to synthesize different composition of  $[Dsim][CF_3COO]/NaY$  composite. For this purpose, the following steps were practiced: (i) NaY zeolite were outgassed at 300 °C for 12 h, (ii) six different weight/weight (w/w) ratios (namely 3, 5, 10, 20, 50 and 80%) of [Dsim] $[CF_3COO]$  ionic liquid and the zeolite powder were added in methanol in a 50 mL round bottom flask, (iii) the suspension was refluxed in methanol for overnight, (iv) the solvent was evaporated in rotary evaporator to get the hybrid acidic catalyst, (v) finally it was treated at 90 °C in vacuum oven for 3 h to remove any traces of unwanted solvent molecule.

# 2.1.2 General Method for the Preparation of 3,4-dihydropyrimidinones Derivatives (4)

A mixture of aromatic aldehyde (1 mmol), ethyl acetoacetate/acetophenone/cyclopentanone (1 mmol) and urea (1.5 mmol) was treated at 60 °C under neat condition (or solvent-less grinding method using mortar and pestle at ambient temperature) utilizing 3 mg of 20% loaded [Dsim] [CF<sub>3</sub>COO]/NaY composite for the appropriate time until the reaction was complete. The progress of the reaction was monitored with thin layer chromatography in presence of EtOAc and petroleum ether (1:2) as mobile phase. The mixture was diluted with hot ethanol (3 mL) to dissolve the crude product. The catalyst was recovered as pure solid residue after filtration of ethanol solution and then washed three times with hot ethanol. The product was isolated as solid precipitate after addition of water to the ethanol solution with vigorous stirring. Recrystallization of the crude product from saturated ethanol gave analytically pure product.

# **3** Results and Discussion

### 3.1 Powder XRD Analysis

Figure 1 is presented for comparative studies of PXRD profile of the parent zeolite (a) and six samples of the [Dsim] [CF<sub>3</sub>COO]/NaY composites with different loading of 3% (b), 5% (c), 10% (d), 20% (e), 50% (f) and 80% (g) respectively in ascending order. The intensity of basic peaks of NaY zeolite gradually decreases against increasing loading of acidic [Dsim][CF<sub>3</sub>COO] up to 20% (e) composite with complete retention of parent structure of zeolite. The



**Fig. 1** Powder XRD profile of the parent and the [Dsim][CF<sub>3</sub>COO] encapsulated NaY zeolite samples: *a* NaY; *b* [Dsim][CF<sub>3</sub>COO]/ NaY=3%; *c* [Dsim][CF<sub>3</sub>COO]/NaY=5%; *d* [Dsim][CF<sub>3</sub>COO]/ NaY=10%; *e* [Dsim][CF<sub>3</sub>COO]/NaY=20%; *f* [Dsim][CF<sub>3</sub>COO]/ NaY=50%; *g* [Dsim][CF<sub>3</sub>COO]/NaY=80%

original structure of zeolite was destroyed above 20% (e) loading in case of 50% (f) and 80% (g) composites which may be due to acidic IL induced dealumination of Y-zeolite to some extra framework Al species in presence of higher amount of ionic liquid. Partial dealumination converted a small portion of the crystalline zeolite structure into amorphous state with significant retention of the crystallinity up to the loading 20% (e) which is reflected in Fig. 2 through comparison of percent crystallinity of modified samples with the parent zeolite. The relative crystallinity differences of four different composites (b, c, d, e) and the parent zeolite (a) were calculated by taking four high intensity peaks at  $2\theta$ =15.54°, 23.54°, 26.90° and 31.28° using Eq. 1 as follows:

% Crystallinity = 
$$(A_S \times 100)/A_R$$
 (1)

where  $A_R$  is integrated area of the reference material under the peaks between a set of 2 $\theta$  limits,  $A_S$  represents integrated area of the sample under the peaks between the same set of 2 $\theta$  limits as that of the reference.

### 3.2 FT-IR Analysis

Figure 3 displays the IR spectra of NaY zeolite and six composites within the range of  $1800-400 \text{ cm}^{-1}$ . The IR spectra of four composites up to 20% loading (e) also showed slight shifting of fundamental absorption peaks of NaY zeolite with preservation of the basic framework. This observation again confirmed that the loaded amount of  $-SO_3H$  functionalized IL for four composites (b, c, d,

**Fig. 2** Comparison of the percent crystallinity of modified samples with the parent zeolite





**Fig. 3** FT-IR profile of the parent and the [Dsim][CF<sub>3</sub>COO] supported NaY zeolite samples: *a* NaY; *b* [Dsim][CF<sub>3</sub>COO]/NaY=3%; *c* [Dsim][CF<sub>3</sub>COO]/NaY=5%; *d* [Dsim][CF<sub>3</sub>COO]/NaY=10%; *e* [Dsim][CF<sub>3</sub>COO]/NaY=20%; *f* [Dsim][CF<sub>3</sub>COO]/NaY=50%; *g* [Dsim][CF<sub>3</sub>COO]/NaY=80%

e) was not enough for complete destruction of Y-zeolite framework via dealumination process. This observation suggests the maximum permissible loading of the IL to be 20% over NaY zeolite.

The peak at 1640–1638 cm<sup>-1</sup> for all the composites can be assigned for bending vibration of water molecule attached to the zeolite structure which is overlapping with -C=N- stretching vibration of imidazolium cation [32]. The fundamental symmetric and asymmetric T–O (Si or Al) stretching vibrations of TO<sub>4</sub> unit of zeolite appeared at 796–784 and at 1026–1011 cm<sup>-1</sup> as weak to strong

 Table 1
 Calculation of Si/Al ratio from IR spectra up to 20% loading composites

Sample name	$v_{DR} (cm^{-1})$	Si/Al ratio
NaY	568	1.93
$[Dsim][CF_3COO]/NaY = 3\%$	572	2.16
$[Dsim][CF_3COO]/NaY = 5\%$	572	2.16
$[Dsim][CF_3COO]/NaY = 10\%$	580	2.74
$[Dsim][CF_3COO]/NaY = 20\%$	584	3.13

bands respectively for the composites (b, c, d, e). The asymmetric T-O (Si or Al) band becomes wider in case of 50% (f) and 80% (g) loaded composites and showed another distinct band at 1246 cm<sup>-1</sup> by merging of S-O symmetric and asymmetric stretching vibration of -SO<sub>3</sub>H groups at 1222 and 1075 cm<sup>-1</sup> [31]. The framework sensitive double-ring vibration peak of TO<sub>4</sub> unit at 568 cm<sup>-1</sup> shifted to around 572-584 cm<sup>-1</sup> for the (b), (c), (d) and (e) composites [33]. In case of highest loaded composites i.e. (f) and (g), we observed the appearance of a small hump at 628–632 cm<sup>-1</sup> for S–O bending vibration of -SO<sub>3</sub>H group along with T-O-T bending vibration. These two composites witnessed the maximum dealumination state in presence of highest amount of acidic IL through collapsing of the basic double-ring vibration and bending vibration of TO<sub>4</sub> building block at 455-458 cm<sup>-1</sup> [34]. The substantial change of absorption patterns of highest loaded composites 50% (f) and 80% (g) revealed the existence of large number of extra framework Al species within these modified zeolite samples [34, 35]. From the double-ring vibration peak of various samples, we calculated the Si/Al ratio of different composites of  $[Dsim][CF_3COO]/NaY$  (Table 1) using the empirical relation (Eq. 2) as proposed by Rüscher et al. [36].

$$\mathbf{x} = 3.857 - 0.00619 \, v(_{\rm DR}) \, (\rm cm^{-1}) \tag{2}$$

where Si/Al = (1-x)/x.

The shifting of this band towards higher wavenumber in case of higher percentage of the ionic liquid loaded composites supports partial modification of the zeolite framework to some EFAI species.

The partial preservation of zeolite framework at high temperature was evidenced from FT-IR spectra of the 20% (e) loaded composite at three different temperatures 250,



**Fig. 4** FT-IR spectra of the composite:  $[Dsim][CF_3COO]/NaY = 20\%$  (e) calcined at 250, 350 and 450 °C respectively



**Fig. 5 A, B** TGA profile of the parent and the  $[Dsim][CF_3COO]$ encapsulated NaY zeolite samples: *a* NaY; *b*  $[Dsim][CF_3COO]/$ NaY=3%; *c*  $[Dsim][CF_3COO]/NaY=5\%$ ; *d*  $[Dsim][CF_3COO]/$ 

350 and 450 °C in Fig. 4. The loss of some water molecules associated with zeolite structure was also clearly appeared at high temperature calcination from the gradual decrease of peak intensity of O–H bending vibration at 1643 cm<sup>-1</sup> of Y-zeolite (Supporting info. Fig. S1).

From the IR study, we can infer that during the preparation of composites:  $[Dsim][CF_3COO]/NaY$ , the basic zeolite framework was modified to some extent with the formation of extra framework species of Al up to the loading of 20% (e). Above that extensive dealumination collapsed the basic structure of NaY in case of (f) and (g) which was reflected in the IR spectra in the Fig. 3.

### 3.3 TGA Analysis

The comparative thermogravimetric analysis of the parent zeolite, the hybrid materials and the ionic liquid are presented in Fig. 5A, B. In the Fig. 5A, the TGA profile of NaY (a), 3% (b), 5% (c) loaded samples shows approximate 18–20% weight loss around 100 °C without any further decomposition up to 600 °C which can be accounted for loss of only Na<sup>+</sup> bound water or physisorbed water from the zeolite framework [37]. The amount of such water gradually reduces to 10–12% in case of 10% (d) and 20% (e) loaded composites as evident from TGA plot in the Fig. 5B. Partial dealumination caused by  $-SO_3H$  moiety imparts a stabilizing effect in case of (d) and (e) composites by healing of Al defects with migrating H<sub>4</sub>SiO<sub>4</sub> molecules [38].

On the other hand, both the curves of 50% (f) and 80% (g) loaded composites displayed 25% (approx.) weight loss in two steps below 150 °C followed by continuous weight loss up to 600 °C. These unusual observations represent a destabilized zeolite framework for these two



NaY = 10%; e [Dsim][CF<sub>3</sub>COO]/NaY = 20%; f [Dsim][CF<sub>3</sub>COO]/ NaY = 50%; g [Dsim][CF<sub>3</sub>COO]/NaY = 80%; h [Dsim][CF<sub>3</sub>COO]

composites in the highest dealumination state caused by the acidic IL during preparation, which is also evident from the IR and PXRD studies. The most probable cause may be the loss of some water molecules from Al defects consisting of four silanols (Si–OH) within the zeolite framework created during the dealumination process [39].

### 3.4 SEM-EDX Analysis

The SEM images portrayed the surface of NaY zeolite to be consisting of perfectly cube shaped particles. As can be seen in Fig. 6, the loaded IL particles form small clusters over the zeolite surface (composites b and e) which reduces the size and uniformity of the zeolite particles. The distribution of such clusters is observed to be more disordered for the 3% loaded composite. We found less clusters on the SEM image of 20% loaded composite with wide scattering of smaller crystallite size partclies. The Y-zeolite structure got completely destroyed in case of highest loaded composite via dealumination of zeolite framework as observed from the IR study.

The EDX spectra of (e) composite showed the presence of constituent elements of  $[Dsim][CF_3COO]$  IL as well as NaY zeolite (Fig. 7).



Fig. 7 EDX spectra of  $[Dsim][CF_3COO]/NaY = 20\%$  (e)

### 3.5 TEM Analysis

The HRTEM imaging in Fig. 8 was carried out for the 20% loaded composite. The TEM images displayed the encapsulation or accumulation of  $[Dsim][CF_3COO]$  on the external surface of zeolite pores with preservation of crystalline structure of Y-zeolite framework in this composite as confirmed from the PXRD pattern in the Fig. 1.



Fig. 6 SEM images of basic zeolite and composites: i NaY; ii [Dsim][CF<sub>3</sub>COO]/NaY = 3%; iii [Dsim][CF<sub>3</sub>COO]/NaY = 20%; iv [Dsim][CF<sub>3</sub>COO]/NaY = 80%





Table 2 Textural properties of NaY zeolite and the composite

Sample name	BET area (m <sup>2</sup> /g) <sup>a</sup>	Micropore volume (cm <sup>3</sup> /g) <sup>b</sup>	Micropore area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g) <sup>b</sup>
NaY(a)	912.6	0.377	900.7	11.92
$[Dsim] \\ [CF_3COO]/ \\ NaY = 20\%$	291.0	0.153	287.4	3.60

<sup>a</sup>Multipoint BET, <sup>b</sup>t-plot method

### 3.6 BET Analysis

The BET surface area measurement was performed for the 20% (e) loaded composite and NaY zeolite to check the change in porosity of the supported material. As evident from the Table 2, the composite witnessed rapid loss in surface area and pore volume compared to the basic NaY zeolite as calculated from t-plot method (Fig. 9) [40]. The abrupt decrease in surface area and micropore volume in case of the 0.2 (e) composite mainly refers to modification of zeolite framework into non-porous surface through

encapsulation of acidic  $[Dsim][CF_3COO]$  which may reduce the access of zeolite pores for adsorption of  $N_2$  gas.

### 3.7 Acidity Determination by Hammett Plot

The Hammett acidity of four acidic composites up to 20% loading was determined from UV-Visible Hammett plot in Fig. 10 according to the standard method using 4-nitroaniline as basic indicator in ethanol solution [41]. The indicator showed maximum absorbance at 378 nm in ethanol. The Hammett acidity was expressed as decreasing order against their observed H<sup>0</sup> values as included in supporting documents (Tables S1-S3): [Dsim][CF<sub>3</sub>COO]/NaY=20% (e) >[Dsim][CF<sub>3</sub>COO]/NaY = 3% (b) > [Dsim][CF<sub>3</sub>COO]/ NaY = 10% (d) > [Dsim][CF<sub>3</sub>COO]/NaY = 5\% (c). The higher acidity of 20% (e) loaded composite can be expected from gaining of extra stabilization through healing effects as mentioned in the TGA analysis (Fig. 5) as well as lower rate of clustering of smaller size particle which is clearly visible in the SEM image (Fig. 6). The unusual order of other three composites 3% (b), 5% (c) and 10% (d) can be accounted for different rate of clustering and their effects on blocking the active sites of composites for interaction



**Fig. 9** I  $N_2$  physisorption Isotherms for NaY and composite (e); II pore size distribution plot for NaY; III pore size distribution plot for composite (e); IV t-plot for NaY; V t-plot for composite (e)



**Fig. 10** Hammett plots of the composites (b)  $[Dsim][CF_3COO]/NaY=3\%$ ; (c)  $[Dsim][CF_3COO]/NaY=5\%$ ; (d)  $[Dsim][CF_3COO]/NaY=10\%$ ; (e)  $[Dsim][CF_3COO]/NaY=20\%$  in three conditions; **A** Hammett plot by mixing equal concentration of the indicator and the

with the basic indicator. The order of Hammett acidity did not change in Fig. 10B, C against the mixing of 1:4 and 2:3 ratio of the indicator and the respective four composite.

### 3.8 Catalytic Performance

To evaluate the activity of the catalysts under different conditions systematically, we choose the three component reaction of ethyl acetoacetate (1 mmol), benzaldehyde(1 mmol) and urea (1.5 mmol) as the model reaction under solvent free condition at different temperatures and the results are presented in Table 3. Due to small difference in acidity of the synthesized catalysts as determined through the Hammett plots (Fig. 10A), we tested the catalytic performance

composites; **B** Hammett plot by mixing 1:4 ratio of the indicator and the composites; **C** Hammett plot by mixing 2:3 ratio of the indicator and the composites

of four composites namely 3% (b), 5% (c), 10% (d) and 20% (e) with 10 mg under solvent-free method at 80 °C. Though there was small difference in the time required for completion of the reaction, the 20% loaded composite afforded the best result (entries 2–4). With the sole IL, it took 15 min to complete the reaction (entry 1). By reducing the amount of 20% loaded composite at 80 and 60 °C (entries 6–8), we observed excellent results in both cases (entry 7, 8) using 3 mg of the composite [Dsim][CF<sub>3</sub>COO]/NaY=20% (e) for 2–10 min reaction.

For the sake of much milder condition to be developed, the reaction was carried out at room temperature using mechanical energy. It only took 15 min to complete the reaction with an excellent yield of 93% (entry Table 3Optimization ofthe reaction condition for thesynthesis of model compound(4a)

Table 4Substrate scope studyfor DHPMs derivatives using20% loaded catalyst

Entry	Catalyst	Amount of the catalyst (mg)	Temp. (°C)	Time (min)	Product yield <sup>a</sup> ( <b>4a</b> ) (%)
1	[Dsim][CF <sub>3</sub> COO]	10	80	10	93
2	$[Dsim][CF_3COO]/NaY=3\%$	10	80	4	94
3	[Dsim][CF <sub>3</sub> COO]/NaY=5%	10	80	7	91
4	[Dsim][CF <sub>3</sub> COO]/NaY=10%	10	80	5	92
5	[Dsim][CF <sub>3</sub> COO]/NaY=20%	10	80	2	97
6	-do-	5	80	2	96
7	-do-	3	80	2	94
8	-do-	3	60	10	96
9	-do-	3	r.t. grinding	15	95

<sup>a</sup>Isolated yields

9). Therefore, we extended our studies for the preparation of other derivatives of DHPMs through variation of aromatic aldehydes and keto compound in presence of 3 mg of 20% (e) loaded catalyst under solvent-free medium at 60 °C and at mild condition using grinding method. All these observations were included in Table 4.

Single crystal X-ray analysis was performed on the 3,4-dihydropyrimidine derivative **4f** (Table 4, entry 6) which confirmed the presence of basic DHPM unit in Fig. 11 [44].

### 3.9 Recyclability Profile of the Catalyst

The recyclability profile of 20% loaded composite (e) was evaluated for the preparation of **4a** from the mixture of 3 mmol of  $\beta$ -keto ester and benzaldehyde with 4.5 mmol of urea under the optimized condition and it was found that the catalyst maintains very good activity up to 6th repetitive cycle (Fig. 12). After the reaction was over, the catalyst surface was washed with cold water and hot EtOH and then it was dried in oven 70°C to make it ready for the next cycles of reactions. With increased number of cycles, the catalyst slowly lost its efficiency which was reflecting in decreasing percentage yields of

Entry	β-ketoester/ketone	Aldehyde	Time (min) (method)		Product yield (%) <sup>a,b,c</sup> (4a–l)	
			A	В	A	В
1	CH <sub>3</sub> COCH <sub>2</sub> COOC <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CHO	10	15	96	93
2	-do-	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	15	18	94	92
3	-do-	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	20	24	92	90
4	-do-	4-OHC <sub>6</sub> H <sub>4</sub> CHO	18	25	93	93
5	-do-	4-ClC <sub>6</sub> H <sub>4</sub> CHO	30	30	94	91
6	-do-	2,4-ClC <sub>6</sub> H <sub>3</sub> CHO	35	35	92	90
7	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CHO	15	30	94	89
8	-do-	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	20	30	89	85
9	-do-	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	15	30	95	92
10	-do-	1-Naphthaldehyde	28	35	85	82
11	Cyclopentanone	C <sub>6</sub> H <sub>5</sub> CHO	25	32	92	87 <sup>d</sup>
12	-do-	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	25	35	93	88

<sup>a</sup>Isolated yields

<sup>b</sup>Method A: reactions were performed at 60 °C, Method B: reactions were conducted using mortar and pestle under solvent-free grinding at ambient temperature

<sup>c</sup>Melting points of known compounds were compared with the literature values in supporting file [26, 27, 42, 43]

<sup>d</sup>Using 2 equivalent of aldehydes



Fig. 11 Single crystal structure of 4f



Fig. 12 Recyclability profile for the composite: [Dsim][CF\_3COO]/ NaY = 20% (e)

expected product with gradual rise of reaction time for completion of the reaction.

### 3.10 Characterization of the Spent Catalyst

The spent catalyst was again subjected for FT-IR analysis (Fig. 13) after every alternate cycle to observe the effect of repeated thermal treatment and washing with hot ethanol on the ratio of Si/Al for dealumination which may slightly decrease the catalytic activity of spent catalyst in next consecutive cycles. Table S4 in supporting file shows the retention of initial Si/Al ratio up to 4th cycle after that it indicates a higher value of Si/Al ratio due to formation of extraframework Al species from 6th cycle onward.

Likewise, the PXRD pattern of used catalyst (Supporting file, Fig. S2) also displays reduction of peak intensity of the composite material after every alternate cycle which can be attributed for loss of crystallinity of spent catalyst.



Fig. 13 FT-IR spectra for the reused catalyst

## 4 Conclusion

In this study, we analyzed the structural changes of parent NaY zeolite within the framework of modified composites [Dsim][CF<sub>3</sub>COO]/NaY using different analytical techniques from which we identified 20% (e) loading as the best acidic composite from the Hammett function with thermal stability up to 450 °C. Loading above this percentage was harmful for the zeolite framework because of maximum dealumination as evidenced from the FT-IR and PXRD patterns of the 50% (f) and 80% (g) loading. Formation of EFAl species on loading of the acidic IL affected the Si/Al ratio of the composites which in turn may also affect the acidity scale of the composites. The strong acidic composite 20% (e) was examined as heterogeneous catalyst for synthesis of DHPMs derivatives under solvent-free medium at 60 °C and at ambient temperature using solvent-free grinding method.

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- 44. CCDC-1507118 (**4f**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.ac.uk/data/\_request/cif