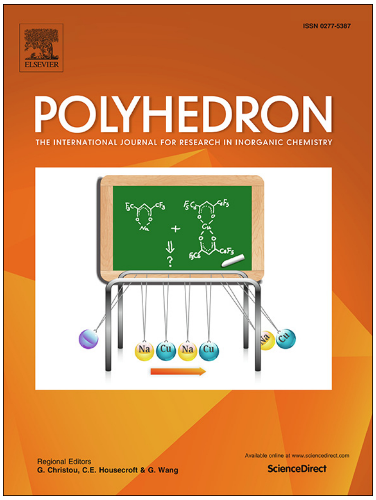

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Samahe Sadjadi, Maryam Akbari, Fatemeh Ghoreyshi Kahangi, Majid M. Heravi

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Acidic polymer containing sulfunic acid and carboxylic acid groups heterogenized with natural clay: a novel metal free and heterogeneous catalyst for acid-catalyzed reactions

Samahe Sadjadi[*a], Maryam Akbari[b], Fatemeh Ghoreyshi Kahangi[c], Majid, M. Heravi[b]*

[a] Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemicals Institute, PO Box 14975-112, Tehran, Iran. Tel.: +982148666; Fax: +982144787021-3; E-mail: samahesadjadi@yahoo.com and s.sadjadi@ippi.ac.ir

[b]Department of Chemistry, School of Science, Alzahra University, PO Box 1993891176, Vanak, Tehran, Iran. Tel.: +98 21 88044051; fax: +982188041344; E-mail: mmh1331@yahoo.com and m.heravi@alzahra.ac.ir

[c] Department of Chemistry, University Campus 2, University of Guilan, Rasht, Iran

Abstract

A novel metal-free solid acid catalyst, PHSA, has been designed and synthesized through facile and environmentally benign procedure via using halloysite nanoclay as a natural and biocompatible support. The synthetic protocol included co-polymerization of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in the presence of vinyl functionalized halloysite. The metal-free solid catalyst that contained both carboxylic acid and sulfonic acid functionality exhibited high catalytic activity for catalyzing both Knoevenagel condensation and Xanthenes synthesis under mild reaction conditions in aqueous media. The presence of halloysite in the structure of PHSA rendered the catalyst heterogeneous and facilitated its recovery and recyclability compared to the halloysite-free homogeneous counterpart. High catalytic activity and recyclability of the catalyst, simplicity of the preparation procedure, using available and natural clay as a support are the merits of this new metal-free solid acid catalyst.

Keywords: Halloysite**,** Polymer, Metal free catalyst, Knoevenagel condensation, Xanthenes.

1. Introduction:

Environmental considerations and safety concerns have motivated researchers to find solid acids as alternatives for corrosive and hazardous liquid-acid catalysts. Although traditional liquid-acid catalysts are highly efficient, they are difficult to separate from the homogeneous reaction mixture, resulting in non-recyclable acid waste. Acidic polymers are solid acids that can effectively catalyze a wide range of organic reactions. Many organic reactions can be typically promoted by acid catalysts, including synthesis of α,β-unsaturated materials and Xanthene. The Knoevenagel condensation is the general and primitive route for the synthesis of α,β-unsaturated compounds by condensation of aldehydes or ketones with a C–H acidic methylene group-containing compounds [1]. It is also regarded as a key step for the synthesis of fine chemicals, therapeutic drugs (e.g. niphendipine and nitrendipine) and functional polymers [2]. Xanthenes are also fertile sources of biologically important molecules possessing various important pharmacological properties such as antiviral, antibacterial and anti-inflammatory [3, 4]. In addition, Xanthene derivatives are one of the most important classes of drugs in photodynamic therapy and antagonists for paralyzing the action of zoxazolamine [5, 6]. Furthermore, extensive studies have revealed that these compounds exhibit many other range of applications from utilizing as dyes, pH-sensitive fluorescent materials for the visualization of biomolecular assemblies and laser technology [7]. Consequently, development of various protocols for the synthesis of

Xanthene derivatives, particularly based on the use of heterogeneous catalysts has been found as the subject of research of some organic and medicinal chemists in recent years. To date, several catalysts have been reported for Knoevenagel condensation, including $TiCl_4$ [8], MOF [9], polyacrylonitrile fiber [10] and amine functionalized montmorillonite [11]. Synthesis of Xanthenes has also been promoted by using various catalysts such as TiO_2-SO_3H [12], ionic liquid [13] and acid functionalized SiO_2 [14-16].

Although the abovementioned catalytic routes have provided significant achievements, some of the methods are plagued by some limitations in terms of yields, long reaction times, and excess of organic solvent, high temperatures, harsh reaction conditions and catalyst reusability. Considering the great achievements of metal-free catalyzed reactions over the past decade and the intrinsic advantages of these catalysts compared to metal catalysts such low cost, development of new solid acids is of interest.

Halloysite clay (Hal) is a tubular natural clay with chemical composition similar to Kaolin [17]. The discovery of this clay dated back to many years ago. However, it has received tremendous attention in recent decade and research groups disclosed its utilities for catalysis, cleaning, material science and drug delivery [18-26]. Hal can be applied both in its bare form and composite with other compounds such as dendrimers and polymers. Moreover, the properties of Hal can be tuned via surface functionalization [27].

Pursuing our research on the development of heterogeneous Hal-based catalysts [28, 29], herein, we disclose the synthesis of a novel metal-free acidic catalyst, PHSA, using Hal as a biocompatible, naturally occurring and available clay. The catalyst has been prepared through co-polymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylic acid (AA) in the presence of vinyl functionalized Hal. The catalyst that possessed both carboxyl acid and -SO_3H

groups showed high catalytic activity for promoting two types of acid catalyzed reactions, Knoevenagel condensation and synthesis of Xanthenes. Compared to Hal-free counterpart, PHSA was heterogeneous and could be recovered and recycled easily for five reaction runs.

2. Experimental

2.1. Materials

The materials applied for the synthesis of the catalyst included, acrylic acid (AA), Hal, ammonium persulfate (APS), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and vinyltrimethoxysilane. To evaluate the catalytic activity of the catalyst, two organic transformations, i.e. synthesis of Xanthenes and Knoevenagel condensation were targeted. To perform these reactions, aldehydes, malononitrile and dimedone were utilized. All the chemicals and solvents used for this research were provided from Sigma-Aldrich and used as received.

2.2. Instruments

To confirm the formation of the catalyst, PHSA, it was analyzed via XRD, TGA, SEM, TEM, BET, TPD and FTIR. The FTIR spectrum of PHSA was recorded by using PERKIN-ELMER-Spectrum 65 instrument. The used XRD instrument was Siemens, D5000. Cu Kα radiation from a sealed tube. To investigate the thermal stability of PHSA, its thermogram was recorded via METTLER TOLEDO thermogravimetric analysis apparatus. The TG analysis was performed under inert atmosphere and scanning rate of 10 °C.min^{-1}. The textural features of the PHSA was studied by accomplishing BET analysis using a Belsorp Mini II instrument. In this analysis, the catalyst was degassed at 100 °C for 2 h. SEM images of PHSA were recorded via a Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV. Transmission electron microscope (TEM) images of the catalyst were obtained using a CM30300Kv field emission transmission electron microscope.

2.3. Synthesis of the catalyst

2.3.1. Vinyl functionalization of Hal: synthesis of Hal-V

In order to functionalize Hal surface, Hal (1g) was dispersed in dry toluene (30 mL) via ultrasonic irradiation for 15 min (power 100 W). Then, vinyltrimethoxysilane (2 mL) was slowly added to the abovementioned suspension and the resulting mixture was refluxed under inert atmosphere for 24 h. At the end of the reaction, the precipitate was simply separated via filtration and washed three times with dry toluene. The purified product was then dried in oven at 100 °C for 12 h.

2.3.2. Synthesis of PHSA

To synthesis the catalyst, PHSA, AMPS (1 g) and Hal-V (1 g) were dissolved in 25 mL of distilled water. Subsequently, APS aqueous solution (0.1 g in 5 mL H_2O) as an initiator was added in a dropwise manner into the reaction mixture. After 30 min, AA (1g) was added slowly into the mixture and then the resulting mixture was stirred for 24 h at 50 °C. After the completion of the reaction, the mixture was precipitated using large volume of acetone at room temperature. The obtained PHSA was washed at least two times to remove the unreacted monomers and then dried in oven at 100 °C. Noteworthy, to synthesis the control catalyst, PSA, the same procedure was followed, except, Hal-V was not applied. The procedures of the synthesis of the catalyst and control catalyst are depicted in Figure 1.

2.4. Evaluation of catalytic activity:

2.4.1. Knoevenagel condensation:

In a typical procedure, a mixture of aldehyde (1 mmol), malononitrile (1.2 mmol), catalyst (0.03 g) and H_2O (3 mL) was stirred at ambient temperature for 2 h. At the end of the reaction (monitored by TLC), EtOH (20 mL) was introduced and the catalyst was separated via simple filtration. To reuse PHSA, it was washed with ethanol and water and dried at 100 °C in an oven. The purification of the resulting product was accomplished by recrystallization from EtOH. The physical and spectral data of the compounds were in agreement with those of the authentic samples, Figures S1-S17.

2.4.2. General procedure for the synthesis of 1,8-dioxo-octahydroxanthenes derivative:

Typically, aldehyde (1 mmol), dimedone (2 mmol), catalyst (0.03 g) were mixed in H_2O (3 mL) as solvent. The resulting mixture was then stirred at room temperature for 3 h. After completion of the reaction (traced by TLC), EtOH (20 mL) was added to the reaction mixture and PHSA was filtered. The product was purified by recrystalization from EtOH to afford the pure products in good to high yields.

Figure 1.

3. Result and discussion

3.1. Verification of PHSA formation

To verify the formation of PHSA, it was subjected to XRD analysis. As illustrated in Figure 2, the XRD patterns of PHSA and pristine Hal are similar and both showed the bands at $2\theta = 11.5°$, 20.2°, 26.7°, 35.4°, 55.6° and 62.1° that are the characteristic bands of Hal, JCPDS No. 29-1487 [30, 31]. Notably, the comparison of the XRD patterns of Hal and PHSA showed the lower intensities of the bands of the latter. According to the literature, this issue can be assigned to the presence of polymeric counterpart [32]. It is worth noting that the absence of any shift or displacement of the characteristic bands PHSA compared to Hal can indicate that the polymeric chain did not penetrate into the Hal lumen [27].

Figure 2.

To further verify the formation of PHSA, the TG analysis was performed. First, to confirm the functionalization of Hal with silane, the thermogram of PHSA was recorded and compared with that of Hal Figure 3. As shown, the thermal stability of Hal is slightly higher than that of Hal-V. More precisely, Hal-V showed three weight losses at 170, 320 and 540 °C, related to the loss of the structural water, decomposition of silane group and Hal dehydroxylation respectively [33, 34], while Hal showed only two losses due to the loss of water and dehydroxylation. Comparing these two thermograms, the content of silane functionality on Hal was measured to be ~ 4 wt%. Subsequently, the thermogram of PHSA was recorded. As shown the thermal stability of PHSA was lower than that of Hal and Hal-V and showed an additional weight loss step (about 340 °C) due to the decomposition of polymeric component. The content of polymer on Hal was calculated to be 15 wt%.

To provide more insight into the role of incorporation of Hal in the thermal stability of polymer, the thermal stability of Hal-free control sample, PSA, was also recorded and compared with that of PHSA, Figure 3. As shown, the incorporation of Hal can dramatically enhance the thermal stability of the final catalyst.

Figure 3.

The FTIR spectrum of PHSA was also recorded and compared with that of PSA and Hal. As shown, the FTIR spectrum of PHSA contained two types of the characteristic bands, i.e. the characteristic bands of Hal and PSA. The characteristic bands of PSA are observed at 3372 cm^{-1} (-

OH), 2900 cm^{-1} (-CH_2), 1737 cm^{-1} (-C=O), 1108 (SO_3^- stretching) and 1039 cm^{-1} (O=S=O stretching in SO_3H) [35] and the characteristic bands of Hal are appeared at 580 cm^{-1} (Al-O-Si vibration), 3695 and 3622 cm^{-1} (inner –OH) and1035 cm^{-1} (Si–O stretching).

Figure 4.

To investigate the effect of functionalization on the textural properties of Hal, the N_2-adsorption desorption isotherms of Hal, Hal-V and PHSA were recorded and compared. From the isotherm of Hal, Figure S18, it was found that the isotherm was of type II and the specific surface area of Hal was 48.1 m^{2}g^{-1}. The measurement of the specific surface area of Hal-V showed that this value (35 m^{2}g^{-1}) for Hal-V was lower than that of Hal. This issue can confirm the conjugation of V on the Hal surface. Notably, the N_2-adsorption desorption isotherm of Hal-V was of type II. The N_2-adsorption -desorption isotherm of PHSA, Figure 5, showed that upon introduction of the polymer, the specific surface area decreased remarkably and reached to 4.9 m^{2}g^{-1}. This observation can confirm the coverage of Hal surface area with polymer. It is worth noting that the isotherm of PHSA was of type II, Figure 5, similar to that of Hal and Hal-V.

Figure 5.

Recording SEM and TEM images, the morphology of PHSA was studied. As illustrated in Figure 6. the Hal tubes are detectable in both TEM and SEM images of PHSA. In the SEM images, it can be seen that incorporation of polymer on Hal can lead to the packing of Hal tubes. This can stem from the interactions between the polymer functionalities. In the TEM image of the catalyst, it can be seen that the Hal tubes are covered with polymer.

Figure 6.

Finally, to investigate the acidic property of PHSA, it was subjected to NH_3-TPD analysis. The temperature programmed desorption of NH_3 (NH_3-TPD) is depicted in Figure 7. As illustrated, PHSA showed two broad peaks distributed in the region of 200-300 °C and 450 - 600 °C, indicating two types of acid sites in PHSA. According to the previous reports [36], the low-temperature desorption peak observed at 200-300 °C confirms the presence of weak acidic sites on the catalyst. On the other hand, the high temperature desorption peak (450 – 600 °C), is representative of the strong acidic sites on PHSA. This observation confirmed the acidic nature of PHSA.

Figure 7.

3.2. Investigation of the catalytic activity of PHSA

To commence the study of the catalytic activity of PHSA, a classic acid catalyst reaction, Knoevenagel condensation of benzaldehyde and malononitrile was targeted. First, the reaction was performed in the absence of the catalyst at room temperature (Table 1, entry 7). The result confirmed the necessity of the use of the catalyst for promoting this reaction. Next, the reaction was carried out under solvent free condition with the use of 30 mg PHSA at room temperature (Table 1, entry 6). As shown, solvent free condition was not efficient condition and moderate yield of the desired product was furnished after 2 h. Repeating this reaction in water as solvent remarkably increased the reaction yield and high yield of the reaction was achieved after 1h (Table 1, entry 5). Prolonging the reaction for 2 h under the aforementioned condition led to the quantitative yield and conversion (Table 1, entry 4). Noteworthy, increase of the reaction temperature lingered the reaction (Table 1, entry 2). Regarding the catalyst amount, use of lower mount of the catalyst (Table 1, entry 3) led to the lower yield of the product and 91% of the product was furnished after 5 h. On the other hand, increase of the used catalyst from 30 mg to 40 mg (Table 1, entry 1) did not accelerate the reaction. Considering all these results, the best reaction condition was use of water as solvent, 30 mg of catalyst at room temperature.

Table 1.

Finding the optimum reaction condition, the contribution of Hal to the catalysis was investigated. To this purpose, the model Knoevenagel condensation was performed in the presence of similar amount of Hal and PSA (Hal free catalyst, see Experimental section) as catalysts under the similar reaction condition. The results, Table 2, showed that Hal in its bare form showed moderate catalytic activity and could promote the reaction to furnish the product in 45% yield. PSA control catalyst, on the other hand, showed similar catalytic activity compared to PHSA. However, PSA was soluble in aqueous media and formed a homogeneous catalyst with tedious recyclability, while, PHSA was heterogeneous and could be easily recovered and recycled. This can confirm that incorporation of Hal can improve the catalytic recovery and recyclability. However, the results showed that the role of Hal is not limited to this extent. In more detail, Hal in its individual form can exhibit the catalytic activity and contribute to the catalysis. For that reason, in PHSA that contained only 15 wt% PSA, the catalytic activity was similar to that of PSA. Taking these results into account, PHSA was selected as the catalyst of the choice.

Table 2.

Motivated by high catalytic activity of PHSA as heterogeneous catalyst, the generality of the developed protocol for the Knoevenagel condensation reaction was studied by using various aldehydes as starting materials. As tabulated in Table 2, it can be concluded that PSHA can efficiently promote the reaction of various substrates with different electronic properties (having electron withdrawing and electron donating groups). Moreover, the heterocyclic aldehydes as well as ketones could tolerate this reaction to furnish the corresponding products in high to excellent yields.

The plausible reaction mechanism for Knoevenagel condensation is depicted in Figure 8. It is postulated that the acidic groups, -SO_3H and –CO_2H, on the structure of PHSA, could activate aldehyde and result in the formation of –SO_3^- and –CO_2^- groups that could activate malononitrile. Subsequently, the reaction of both activated substrates resulted in an intermediate that could tolerate dehydration to form the desired product [37].

Figure 8

Following the study of the catalytic activity of PHSA, it was investigated whether this solid acid catalyst could catalyze other acid-catalyzed reaction. In this line, the synthesis of Xanthene derivatives from reaction of aldehydes and dimedone in the presence of PHSA was examined. Interestingly, the results, Table 3, confirmed that various aldehydes could undergo this reaction in the presence of PHSA (30 mg) in water as solvent to furnish the corresponding products after 3 h in high to excellent yields. Notably, furfural as heterocyclic aldehyde could also tolerate this reaction. However, the reaction time for this substrate was longer (4 h).

Table 3.

To show the merit of this protocol for promoting Knoevenagel condensation and Xanthene synthesis, the catalytic activity of PHSA was compared with some of the previously reported catalysts used for catalyzing these two chemical transformations, Tables 4 and 5.

Comparing the catalytic activity of the catalyst with the reported catalysts for Knoevenagel condensation, Table 4, it can be seen that various catalysts, including metal free and metallic catalysts have been reported for promoting this reaction. As an example of metallic catalyst, PdNi@GO can be mentioned. Despite high catalytic activity, use of precious metal and graphenoxide (GO) as support is not economically and environmentally attractive. Use of metal organic frameworks, MOF (Table 4, entry 1), led to high yield. However, the reaction time was relatively high. On the other hand, the synthesis of MOF is mostly costly and time consuming. Use of bio-based catalysts such as chitosan is environmentally interesting. However, the reaction time was relatively long. Ionic liquids are also efficient for promoting this reaction. However, most of them are homogeneous. Considering all of these results, it can be concluded that PHSA can be classified as an efficient catalyst for Knoevenagel condensation.

Table 4. [38-41]

The comparison of the catalytic activity of PHSA for the Xanthene synthesis with other catalysts also confirmed high catalytic activity of the catalyst. More precisely, compared with silica-bonded S-sulfonic acid, PHSA can promote the reaction at lower reaction temperature and shorter reaction time. $Fe_3O_4@SiO_2–SO_3H$ led to the desired product in high yield in short reaction time. However, the reaction temperature and the used catalyst amount were higher than PHSA. Some metallic catalysts such as Nano-ZnO and Nano-NiO were not efficient for this reaction and led to very low yields. $Fe_2(SO_4)_3.7H_2O$ is another catalyst reported for the synthesis of Xanthenes. The yield of the model product is lower than that of PHSA and the reaction temperature was relatively high. Similarly, the efficiency of n-TSA was lower than PHSA and higher temperature was required for promoting the reaction.

Table 5. [12, 14, 15, 42]

3.3. Recovery of PHSA

The final part of this research is devoted to the study of the recyclability of PHSA. This issue is important from both economic and environmental points of view. The recyclability study followed the standard recycling test. Briefly, PHSA was recovered after the first run of model Knoevenagel condensation and after washing and drying (Experimental section), it was re-used for the next run of reaction. This process was repeated for six consecutive reaction runs under exactly similar reaction condition (the optimum condition). The study of the yield of Knoevenagel condensation after each reaction run disclosed that use of PHSA for the second run of the reaction resulted in the quantitative yield of the desired product and the catalytic activity of PHSA did not decreased. However, further recycling up to five reaction runs led to slight decrease of the catalytic activity. Recycling for the sixth run, however, caused a remarkable loss of the catalytic activity and the desired product was furnished only in 61%, Figure 9.

Figure 9.

To elucidate whether recycling can affect the structure of the catalyst, the FTIR spectrum of the recycled catalyst after six reaction runs was compared with that of fresh PHSA, Figure 10. The comparison of both spectra confirmed that the recycling did not destruct the structure of PHSA and the catalyst was stable.

Figure 10.

To further investigate the recycling effect on the catalyst, the XRD pattern of the recycled catalyst after six runs was recorded and compared with that of the fresh catalyst, Figure 11. As depicted in Figure 11, the catalyst characteristic bands can be observed in the XRD pattern of the recycled catalyst. Moreover, no shift in the position of the bands was observed. This can indicate the fact that PHSA was stable and preserved its structure in the course of recycling.

Figure 11.

It is worth noting that the measurement of the specific surface area of the catalyst after six runs, showed that this value slightly decrease (from 4.9 for the fresh catalyst to 3.1 m^2g^{-1}). To investigate whether recycling can induce any change in the morphology of the catalyst, the SEM image of the catalyst after six runs of recycling was recorded, Figure 12. Similar to the fresh PHSA, in the SEM image of the recycled catalyst the Hal tubes can be observed. However, it can be seen that the recycled catalyst showed more packed morphology.

Figure 12.

To elucidate whether the reagents could adsorb the protons, the pH of the reaction mixture was examined in each reaction cycle. Notably, the fresh catalyst in aqueous media led to the acidic media (pH = 3). Interestingly, upon recycling, the pH of the reaction mixture did not change significantly. This observation ruled out the possibility of adoption of the protons by reagents. Considering the results, the lower catalytic activity of the catalyst after six reaction runs can be attributed to the partial aggregation of the Hal tubes that resulted in lower specific surface area. This may hinder the accessibility of the reagents to the catalytic active sites.

Conclusion

PHSA as a metal free solid acid was simply prepared through vinyl functionalization of Hal followed by co-polymerization of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid in its presence. The study of the catalytic activity of PHSA confirmed its high catalytic activity, superior to that of some of the previously reported catalysts for Knoevenagel condensation and Xanthenes synthesis under mild reaction condition in aqueous media. Noteworthy, use of Hal that is a natural and biocompatible clay in the structure of the catalyst rendered PHSA heterogeneous and easy to recover (it can be recycled for six consecutive reaction runs with slight loss of the catalytic activity). On the other hand, Hal exhibited the catalytic activity and contributed to the catalysis. The present protocol benefits from some advantages including, facile preparation of the catalyst using natural and biocompatible clay, high catalytic activity and recyclability, broad scope of the reaction and environmentally benign reaction condition.

Conflicts of interest

There are no conflicts to declare.

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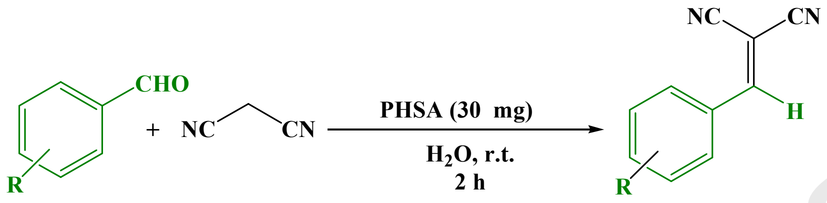
Table 1. The study on the optimum condition of Knoevenagel condensation of benzaldehyde and malononitrile in the presence of PHSA catalyst.

Entry	**PHSA (mg)**	**Solvent**	**Temp. (°C)**	**Time (h)**	**Yield (%)[a]**
1	40	H_2O	r.t.	5	100
2	30	H_2O	60	5	100
3	20	H_2O	r.t.	5	91
4	30	H_2O	r.t.	2	100
5	30	H_2O	r.t.	1	82
6	30	-	r.t.	2	45
7	-	H_2O	r.t.	2	-

[a] Isolated Yield.

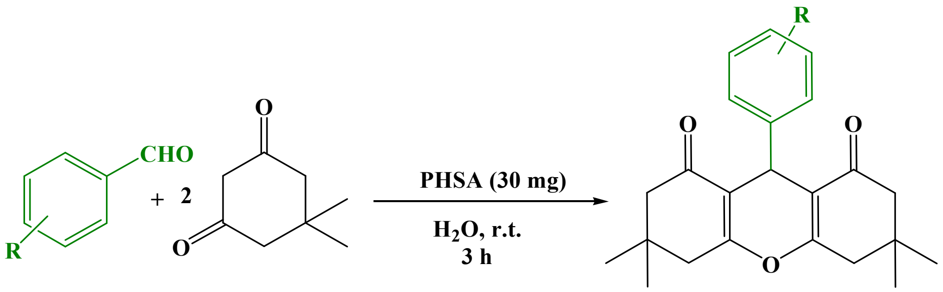
Table 2. Comparison of the catalytic activities of Hal, PSA and PHSA and study of the generality of the PHSA-catalyzed Knoevenagel condensation



Entry	Catalyst	Substrate	Yield (%)
1	Hal	Benzaldehyde	45
2	PSA	Benzaldehyde	100
3	PHSA	Benzaldehyde	100
4	PHSA	4-NO_2-benzaldehyde	100
5	PHSA	3-NO_2-benzaldehyde	96
6	PHSA	4-Me-benzaldehyde	98
7	PHSA	4-MeO-benzaldehyde	94
8	PHSA	2-MeO-benzaldehyde	91
9	PHSA	4-Cl-benzaldehyde	100
10	PHSA	Furfural	90
11	PHSA	Acetophenone [a]	83

[a] 83% in 5h (43% in 2h).

Table 3. Synthesis of various derivatives of Xanthenes under PHSA catalysis.



Entry	Substrate	Yield (%)
1	Benzaldehyde	100
2	4-NO_2-benzaldehyde	100
3	3-NO_2-benzaldehyde	100
4	4-Me-benzaldehyde	96
5	4-MeO-benzaldehyde	100
6	2-MeO-benzaldehyde	93
7	4-Cl-benzaldehyde	100
8	Furfural [a]	91

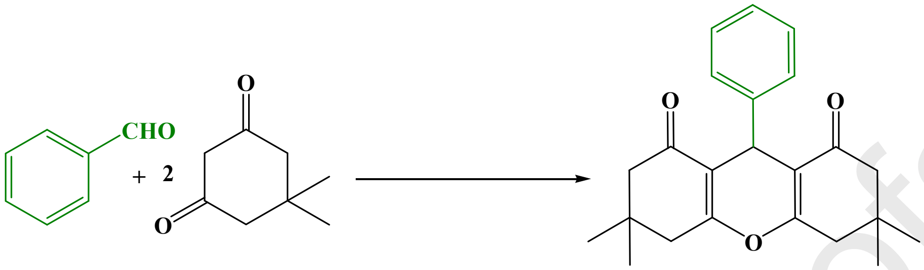
[a] 91% in 4 h (65% in 3h).

Table 4. The comparison of the catalytic activity of PHSA with some of the previously reported catalysts for the synthesis of 2-(phenylmethylene) malononitrile.

Entry	Catalyst [Ref.]	Quantity [a]	Solvent	Temp. (°C)	Time	Yield (%)
1	Activated Hf-UiO-66-N_2H_3[38]	0.02 g	EtOH	r.t.	4h	98
2	PdNi@GO[39]	0.02 g	H_2O/EtOH	25	8 min	95
3	CS[40]	0.025 g	EtOH	40	6h	98
4	$[H_3N^+$-CH_2-CH_2-$OH][CH_3COO^-]$ IL[41]	4 drop	Solvent free	25	<1h	90.9
5	PHSA	0.03 g	H_2O	r.t.	2 h	100

[a] The catalyst quantity was measured for 1 mmol benzaldehyde.

Table 5. The comparison of the catalytic activity of PHSA with some of the previously reported catalysts for the synthesis of 3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2*H*-xanthene1,8-(5*H*,9*H*)-dione.[a]



Entry	Catalyst [Ref.]	Quantity	Solvent	Temp. (°C)	Time h:min	Yield (%)
1	Silica-bonded S-sulfonic acid (SBSSA) [15]	0.03g	EtOH	reflux	10:00	98
2	$Fe_3O_4@SiO_2–SO_3H$ [14]	0.05g	-	110	00.04	97
3	Nano-ZnO [12]	10 mol%	-	100	2:00	Trace
4	Nano-NiO [12]	10 mol%	-	100	2:00	Trace
5	Nano titania-supported sulfonic acid (n-TSA) [12]	0.013g	-	90	1:10	91
6	$Fe_2(SO_4)_3.7H_2O$[42]	10 mol%	-	120	1:30	86
6	PHSA	0.03g	H_2O	r.t.	3:00	100

[a] The catalyst quantity was measured for 1 mmol benzaldehyde.

Author’s contribution

Samahe Sadjadi: Designing the work, writing the manuscript, revising and editing, Financially supporting.

Akbari and Ghoreyshi Kahangi: Doing experiments

Heravi: Partial financial support

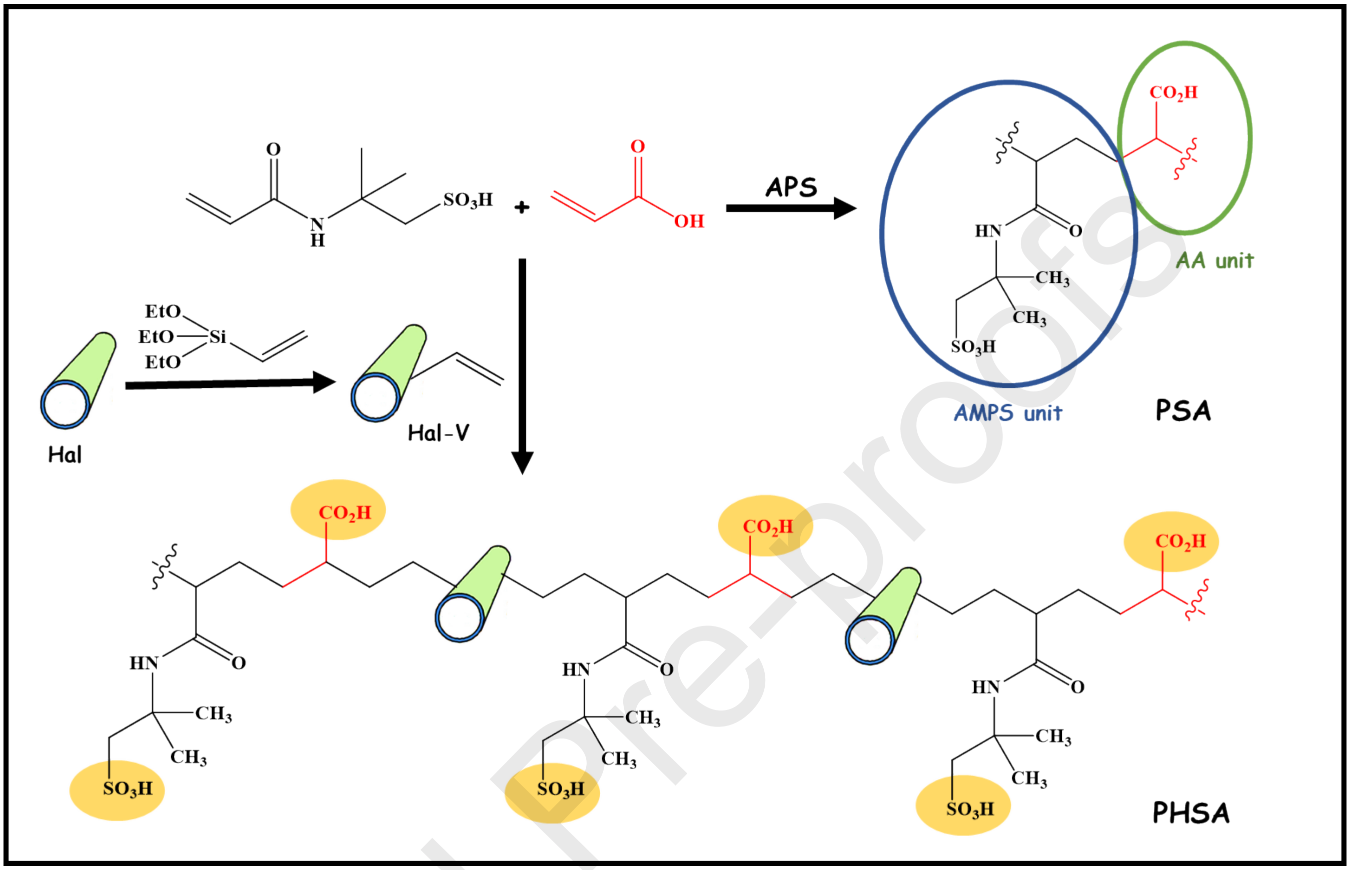


Figure 1. The schematic procedure of the synthesis of PHSA and PSA.

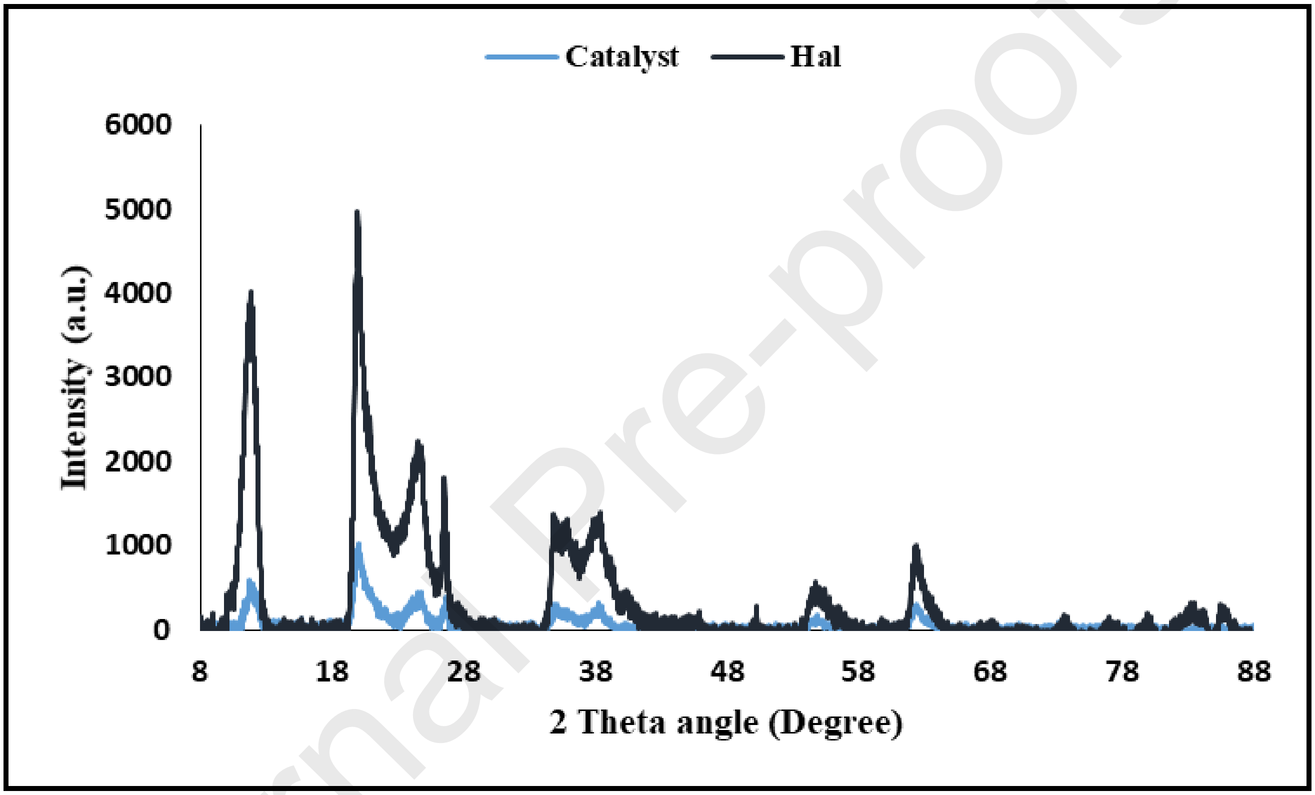


Figure 2. XRD patterns of pristine Hal and PHSA.

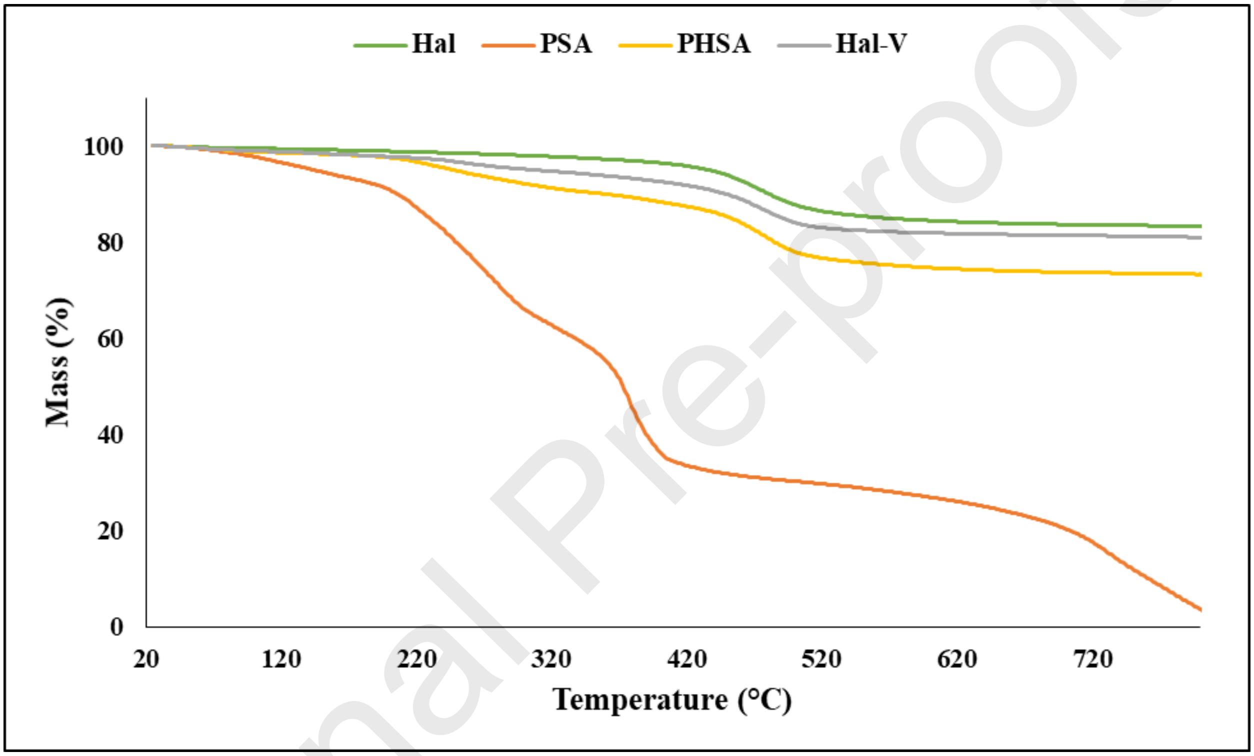


Figure 3. TGA thermograms of Hal, Hal-V, PSA and PHSA.

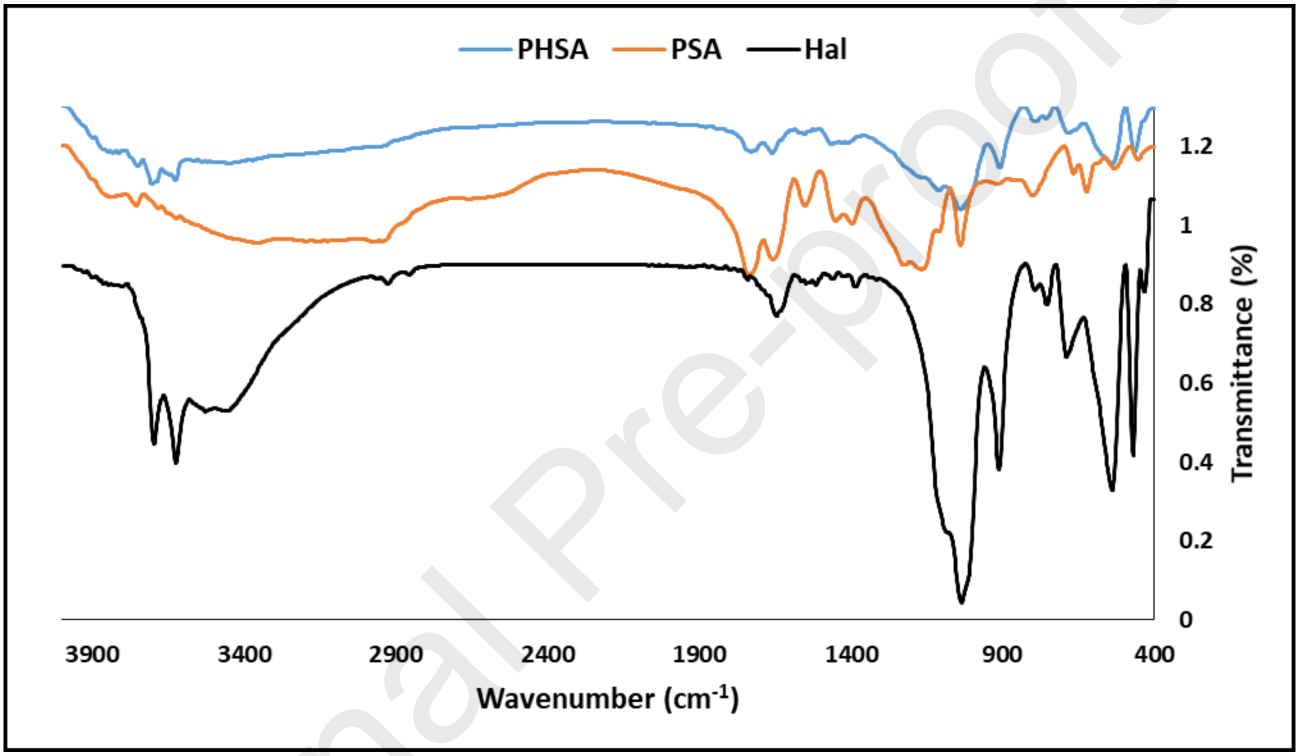


Figure 4. FTIR spectra of Hal, PSA and PHSA.

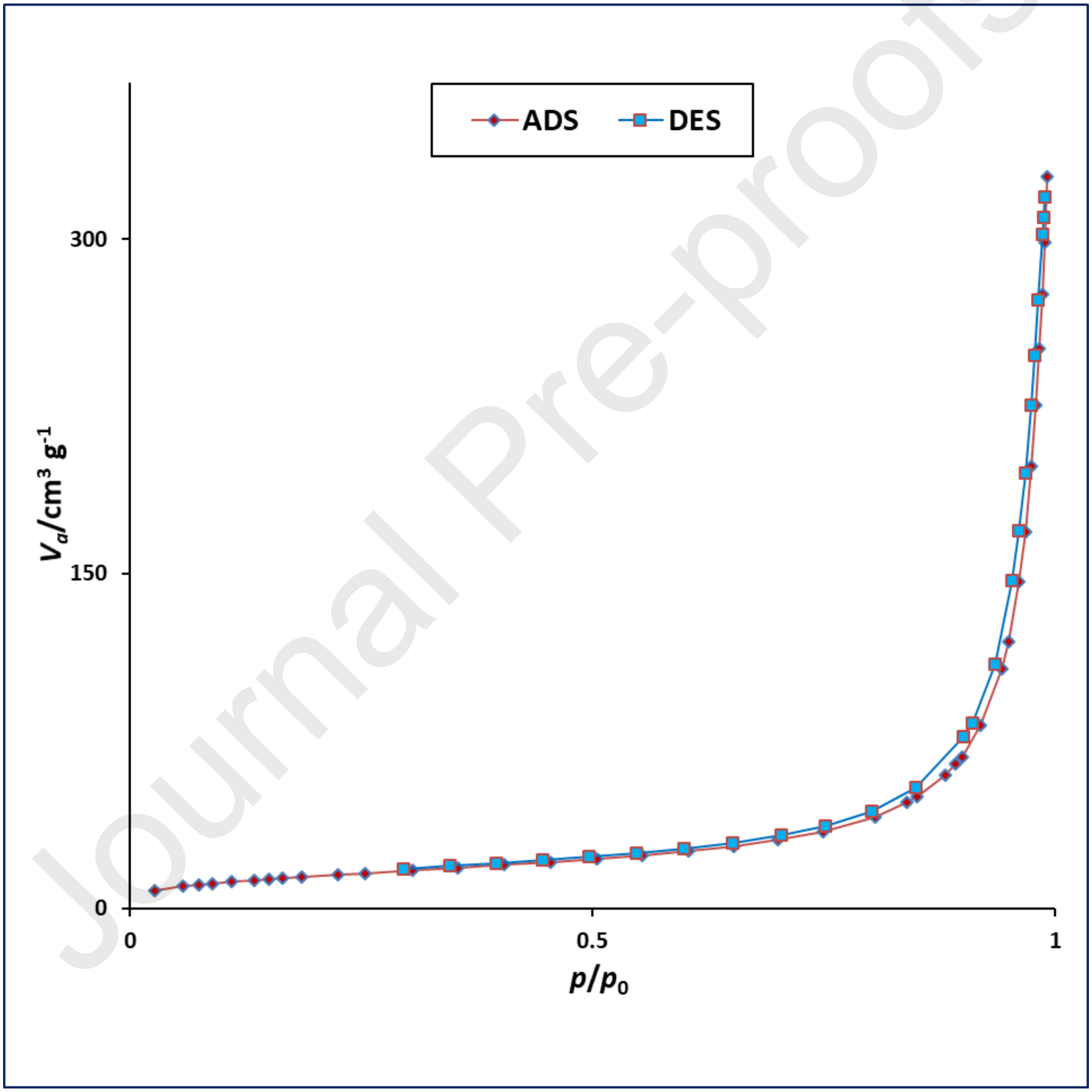


Figure 5. The N_2-adsorption-desorption isotherm of PHSA.

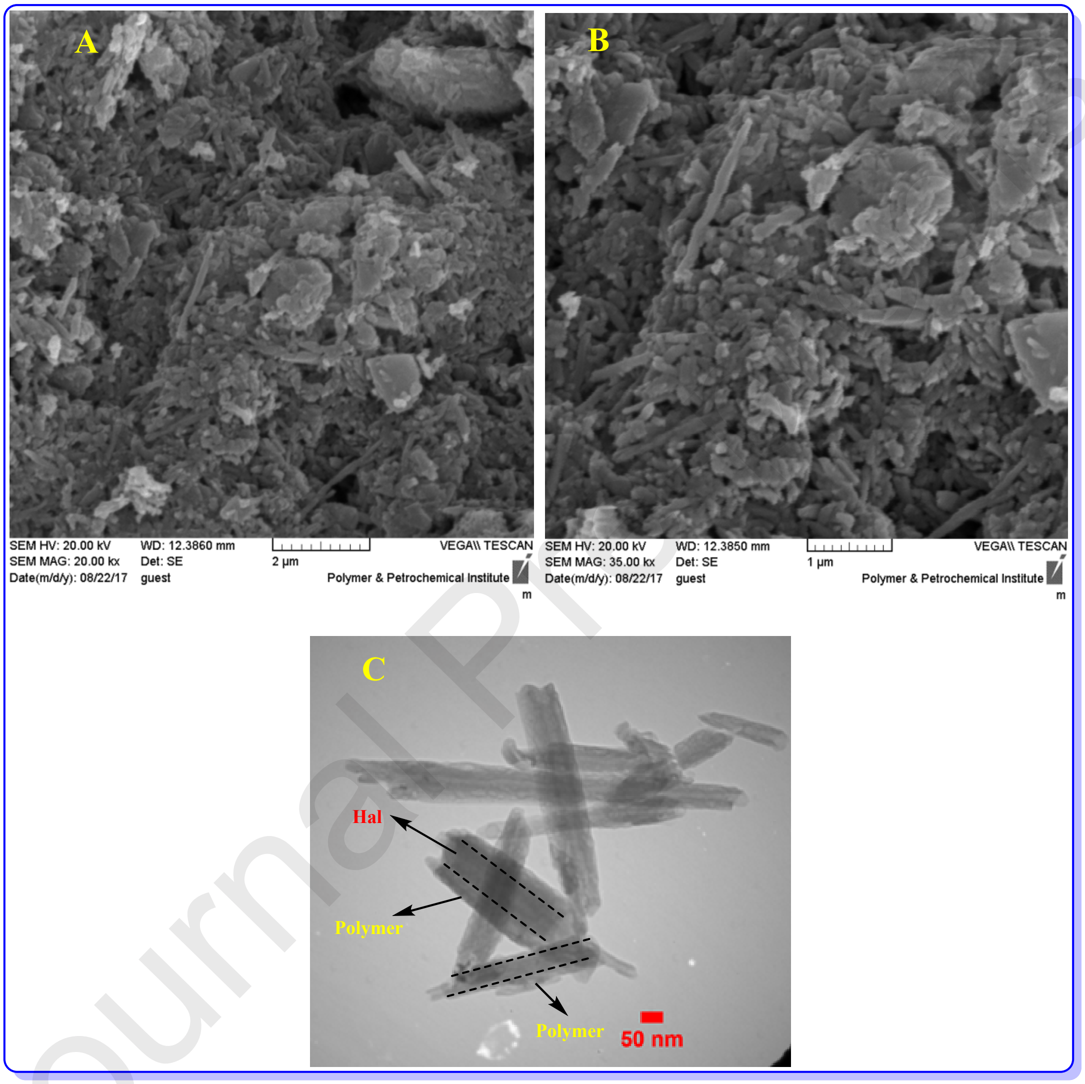


Figure 6. SEM and TEM images of PHSA.

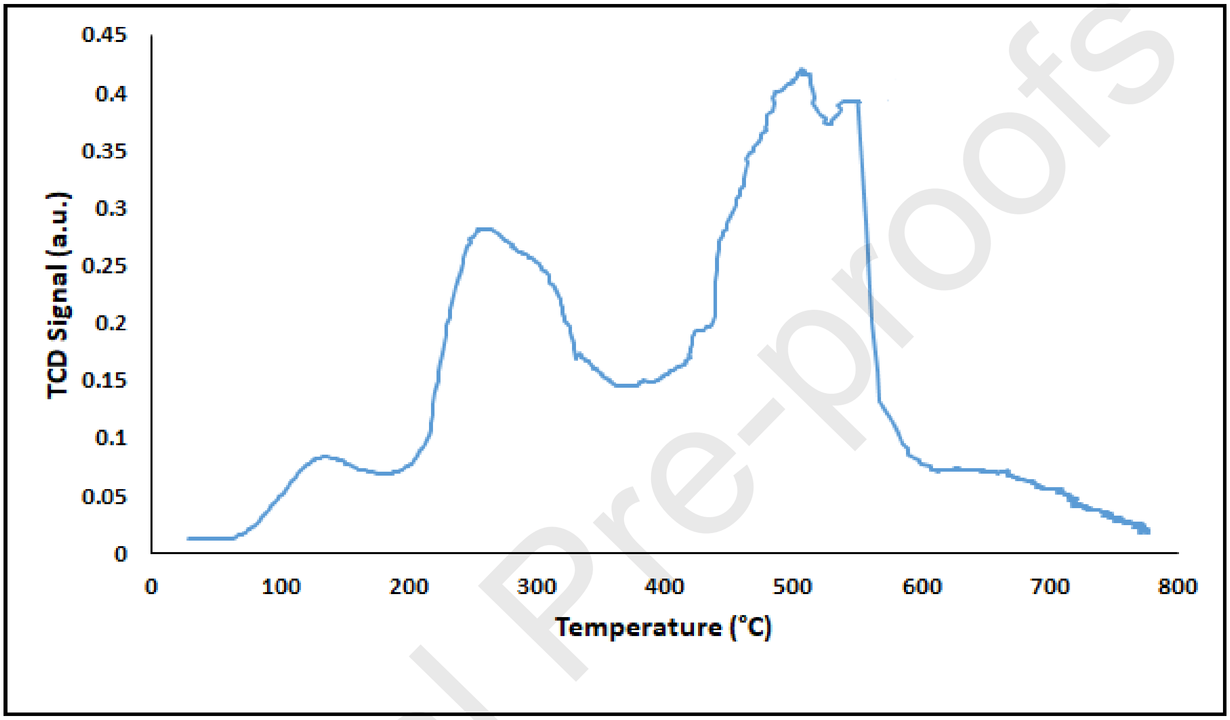


Figure 7. NH_3-TPD analysis of PHSA.

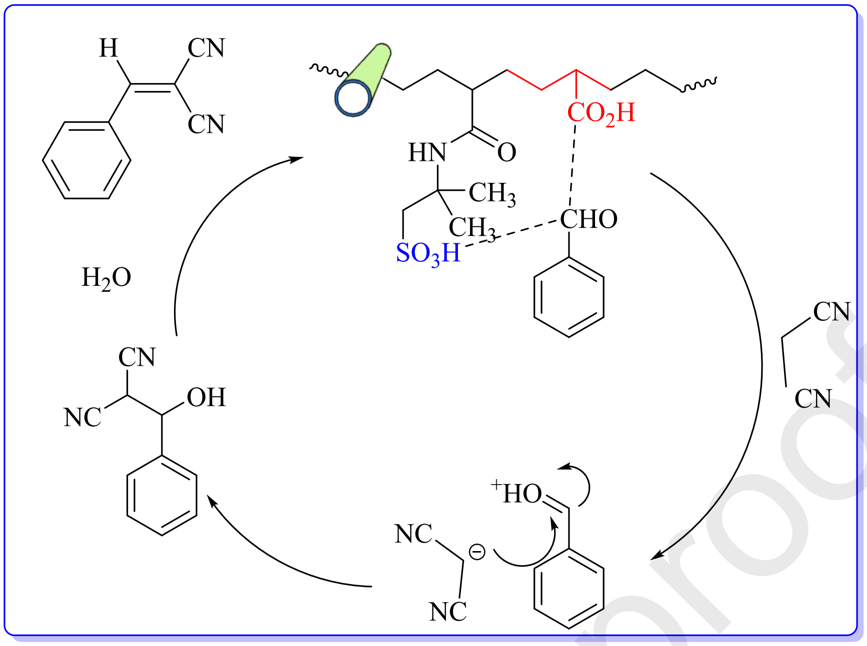


Figure 8. The plausible mechanism for Knoevenagel condensation.

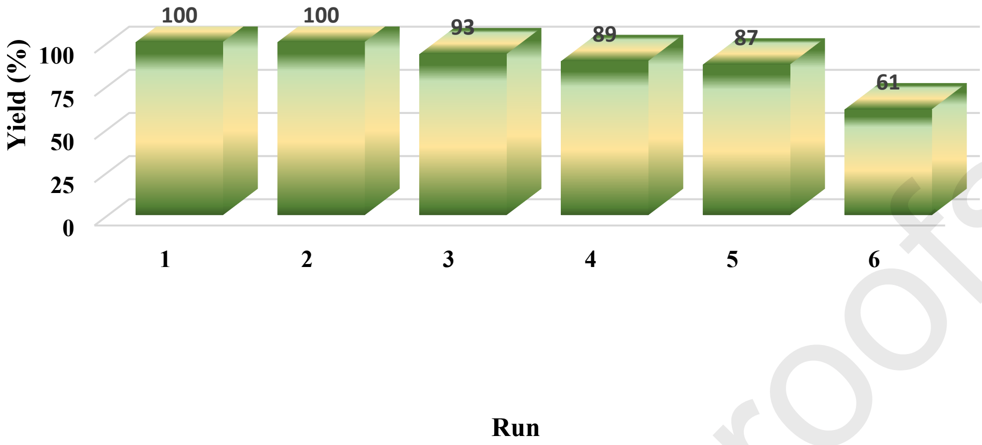


Figure 9. The results of recycling test of PHSA for model Knoevenagel condensation under optimum reaction condition.

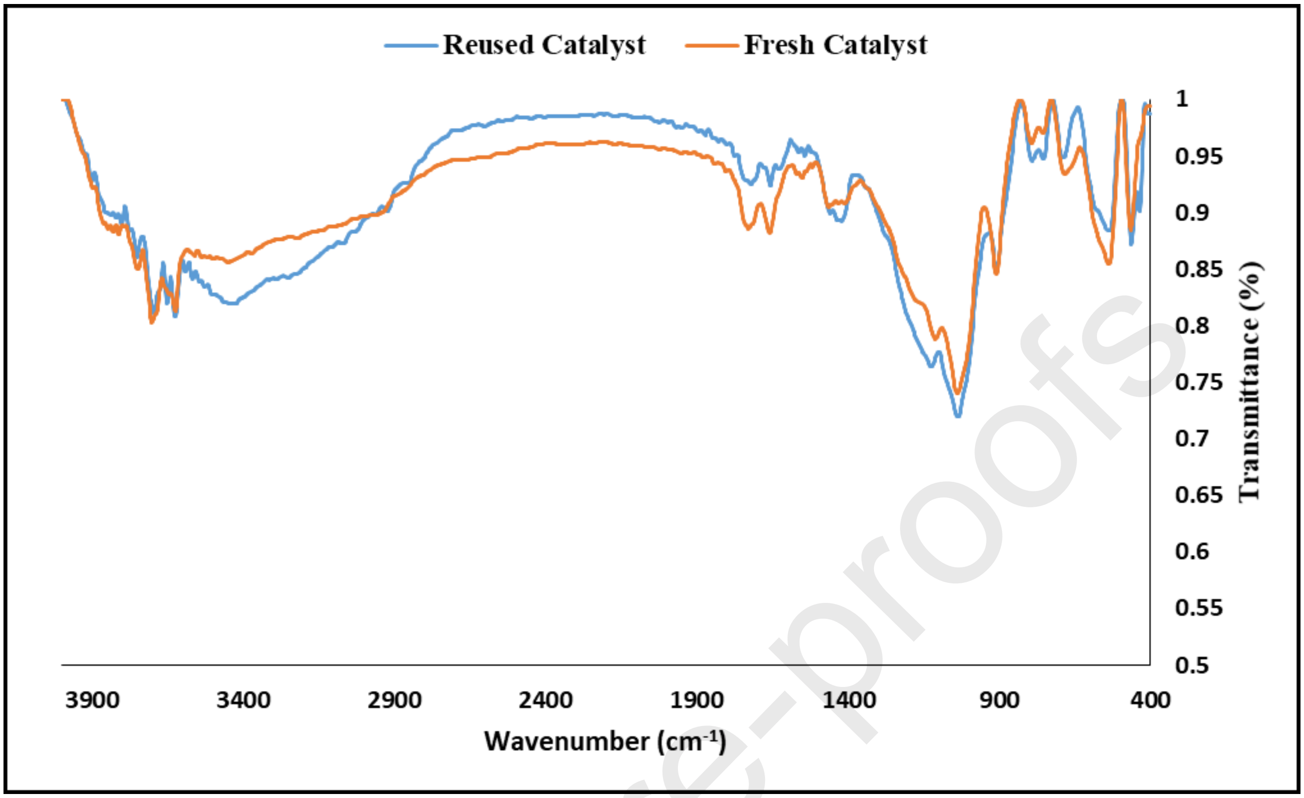


Figure 10. The comparison of the FTIR spectrum of fresh and recycled PHSA after six reaction runs.

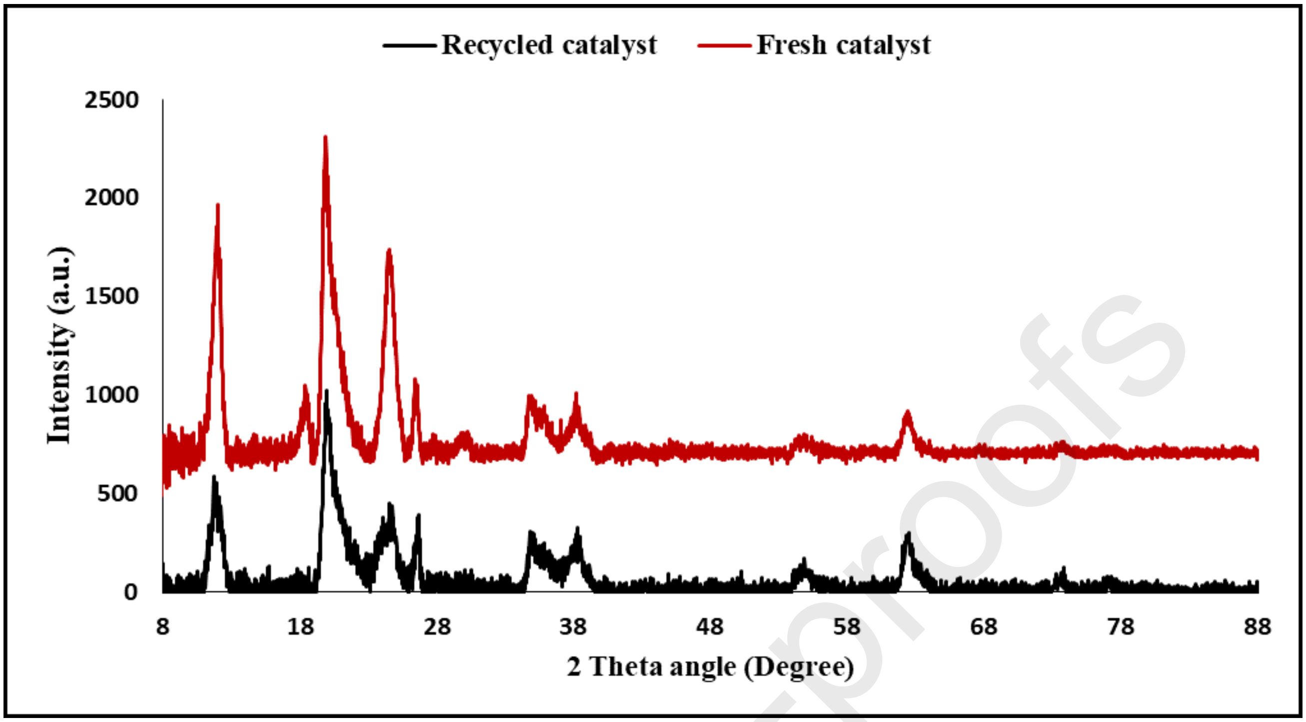


Figure 11. Comparison of the XRD patterns of fresh and recycled catalyst after six reaction runs

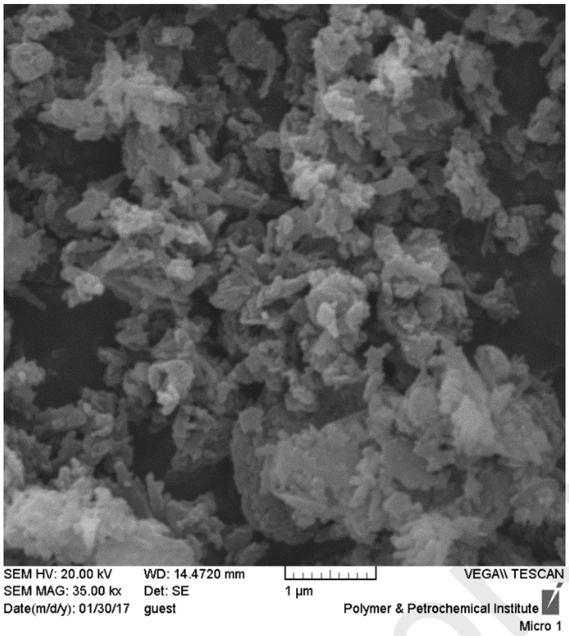
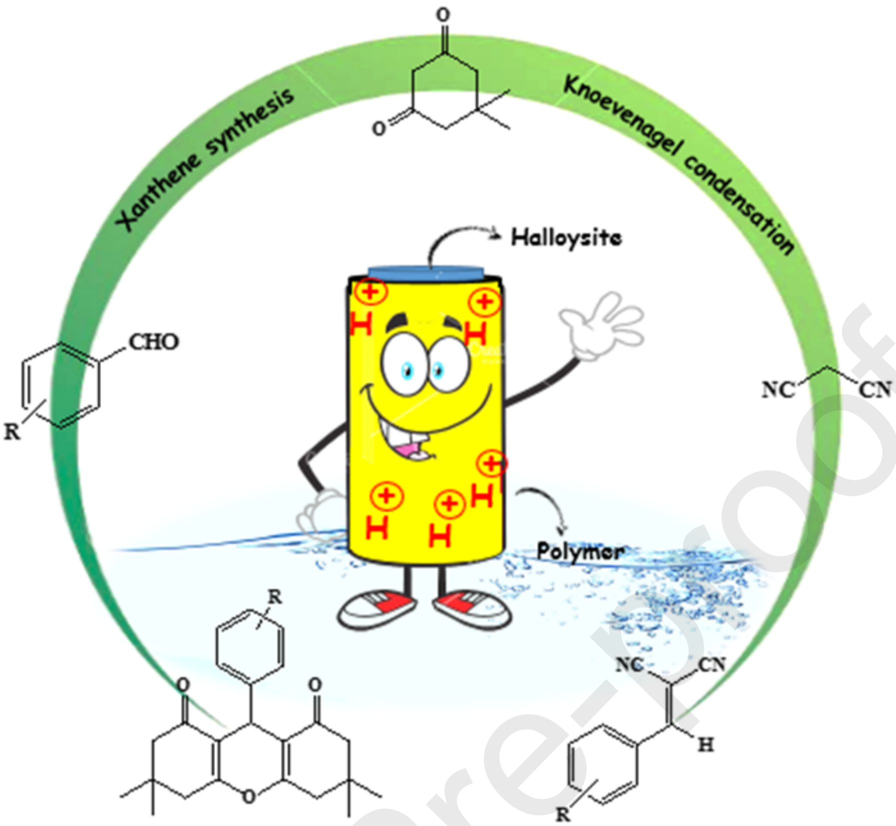


Figure 12. SEM image of the recycled catalyst.


Xanthene synthesis
Knoevenagel condensation
O
O
Halloysite
CHO
R
NC
CN
H
Polymer
R
O
O
O
NC
CN
H
R

Highlight

- A metal-free solid catalyst was developed via decoration of halloysite with polymer.
- The catalyst contained both carboxyl acid and –SO_3H groups.
- The catalyst promoted both Knoevenagel condensation and synthesis of Xanthenes.
- The catalyst was heterogeneous and exhibited high recyclability.