Synthesis and Improving the Crystallinity of a Squaranine Covalent Organic Framework by Investigating the Co-Catalyst Effect and Using It as a green and Metal-Free Catalyst for the synthesis of enaminones

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Research Article

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Abstract

Herein, a modified synthesis method was presented and the effect of using an aqueous acetic acid solution in the process of synthesizing SQCOF was investigated. The addition of a catalytic amount of aqueous acetic acid solution as a co-catalyst has contributed to improved crystallinity quality. Effective parameters of the acid catalyst and the solvent were optimized and the synthesized SQCOF was used as a metal-free catalyst with Bronsted acid groups in the condensation reaction between 1,3-dicarbonyl groups and primary amines. This COF performs excellently as an acidic catalyst with a highly crystalline structure. SQCOF was applied in solvent-free conditions to synthesize enaminones at ambient temperature by gentle manual grinding with a pestle and mortar. High performance and efficiency (62 to 96 %), high TOF (833 to 1283 h\(^{-1}\)), short reaction time, easy workup, elimination of toxic organic solvents, removal of metalated catalysts, and green conditions are the main advantages of this study. SQCOF shows good chemical stability and recyclability (7 runs) and acted as a successful catalyst in the synthesis of enaminones.

1. Introduction

Covalent organic frameworks (COFs) are a novel class of crystalline porous organic polymers formed by covalent interactions between organic monomers with determined topologies that have been used in different fields in recent years [1-6]. High surface area, low density, tunable framework, high crystallinity, and the variety of the available organic monomers, [7-9] make COFs practical and desirable materials in different fields such as water treatment [10,11], membranes [12], sensors [13], catalysis and photocatalysis [14,15], gas and energy storage [16,17], and drug delivery [18]. COFs with different topologies are usually made from reversible linkages such as imine, hydrazone, olefine, borazine, urea, squaraine, etc. [19,20]. COFs are synthesized in two kinetically and thermodynamically controlled steps [21]. In the kinetically controlled step, random and irregular bonds are formed between the building blocks which lead to an amorphous organic framework with faulty connections. In the thermodynamically controlled step, timing, catalyst, and heating can make a profound contribution to correcting faulty reversible bonds and crystalline structures formed [21].

squaraines are organic compounds and dyes that are usually obtained via the condensation of primary amines and squaric acid [22]. squaric acid is a main component of squaranine which can also play the role of an acid catalyst [22]. Therefore, this issue can be generalized to the synthesis of COFs. In some cases, squaric acid has been reported to act as both a building block and a catalyst. squaraine COFs with zwitter ion characteristics have been made from primary squaric acid and primary amines with different topologies [22,23]. These groups of COFs are less developed and used compared to other COFs. The first squaraine-linked COF was synthesized from Copper (II) 5,10,15,20-tetrakis(4-aminophenyl) porphyrin and squaric acid as a mesoporous COF [23]. In another work, ST-COF-1 was produced from melamine and squaric acid and was applied as a sensor [24]. Also, Ding and et.al synthesized many squaraine-linked COFs, utilisable in photothermal studies [22]. Recently, Abbaspourrad and coworkers synthesized and applied SQCOF as a high-performance membrane for water treatment [25].
these reported methods, squaric acid has played the role of an acid catalyst and a monomer. however, in this project, the effect of using acetic acid as a secondary and auxiliary catalyst in the synthesis of SQCOF was investigated. According to the results and optimizations, it seems that the presence of a catalytic amount of aqueous acetic acid can affect the synthesis process, so it can be said that the presence or absence of this catalyst was effective in the synthesis of SQCOF. Also, the addition of this co-catalyst reduced the synthesis time by 4 days, and also the PXRD pattern of the obtained product was closer to the simulated pattern that has been reported [25].

squaranine units in SQCOF can perform as Bronsted acid groups [25] that are placed on the framework through the bottom-up synthesis strategy, without the need for post-modification. So, SQCOF can be a good candidate as a heterogeneous acidic catalyst. Therefore, to investigate the catalytic performance of SQCOF, it was used as a heterogeneous catalyst in the synthesis of enaminones under green conditions.

Enaminones are organic intermediates and compounds with anti-bacterial, anti-cancer, and anti-virus properties [26-28]. Enaminones are important intermediates in the synthesis of organic compounds, biological materials, and nitrogen-containing heterocyclic compounds e.g., pyridine and pyrrole [29-31]. usually, the main strategy for the synthesis of enaminones is a condensation reaction between primary amines and 1,3-dicarbonyl compounds [32,33]. Recently, our group introduced a green continuous method for the synthesis of enaminones in propylene carbonate as a green solvent and CeCl\textsubscript{3}.7H\textsubscript{2}O as a catalyst [34]. Even though, our method has solved many environmental challenges, but it could not be economical because assembling microreactors and flow systems is so expensive [35]. therefore, designing an eco-friendly, heterogeneous catalyst with a green and easy method for the synthesis of enaminones is a crucial matter. In this study, we synthesized and applied SQCOF as a heterogenous catalyst with acidic squaranine blocks and applied it in the synthesis of enaminones in a solvent-free process at ambient temperature using mortar and pestle. so, to investigate the catalyzing properties of SQCOF, this COF was utilized as a metal-free and heterogeneous catalyst for the synthesis of enaminones.

2. Experimental section

2.1. Synthesis of SQCOF:

(4.5 mg, 0.04 mmol) of squaric acid and (12 mg, 0.02 mmol) of 1,3,6,8-tetrakis(4-aminophenyl) pyrene were mixed in a Pyrex tube, and 0.5 ml of 1,4-Dioxane, 0.5 ml of mesitylene, and 100 µl acetic acid (3M) were also added. The suspension was sonicated for 10 min and the slurry was freeze-thaw three times. The tube was then sealed and kept at 120 °C for 3 days. The orange-like solid was filtered and washed with DMF and washed with anhydrous THF for 24 h and dried under vacuum at 100 °C.

2.2. General producer for the synthesis of enaminones:

1 mmol of fresh primary amine and 1 mmol of 1,3-dicarbonyl compound were put in an opal mortar and pestle. Then 7 mg of SQCOF was added and the mixture of reaction was ground for 15 minutes without
stopping. At the end of the reaction, 5 ml of dichloromethane (DCM) was added to the reaction mixture and SQCOF was filtered off. The solvent was evaporated and the crude product was purified by crystallization in hexane and DCM or alternatively via plate chromatography.

2.3. Synthesis of Model-SQ [23]:

\[ p\text{-methyl aniline (0.94 gr, 8.76 mmol) and squaric acid (0.5 g, 4.38 mmol) dissolved in 20 ml of toluene/n-butanol (1:1), and the reaction mixture refluxed overnight. The resulting yellow solid was separated and washed with chloroform to obtain the pure product. (95% Yellow solid). \]

3. Result and discussion

3.1. Optimizations:

In this study, our target was to synthesize SQCOF under common time conditions and temperatures that are usually used for the synthesis of these compounds, therefore, the two parameters of time and temperature were considered fixed at 120 °C degrees and 72 hours, respectively. Therefore, to investigate the catalytic role of acetic acid, the concentration and volume of the aqueous solution of acetic acid as two effective key factors were optimized and the crystallinity of SQCOF was investigated by PXRD. according to previous studies, a sharp peak near 7.85 (in simulated PXRD) [25] is related to crystallinity quality. Therefore, in this study, we used the 8.4 peak, which was close to the mentioned value and is a symbol of the crystallinity of the structure, as the basis for optimization. To achieve the best crystalline structure, different concentrations such as glacial, 3 M, and 10.5 M acetic acid were used and according to Figure 1, SQCOF was synthesized with many different volumes and concentrations of acetic acid. As shown in Figure 1 in the absence of acetic acid, the peak area of 8.4 appeared very weak. By changing the solvent to a mixture (1:1) of dichlorobenzene (DCB) and n-butanol (BOH), these weak peaks are completely removed and the structure becomes amorphous. Glacial acetic acid also leads to the production of an amorphous structure, which is proof of the role of water and acid together in the formation of the crystalline structure, adding 100 microliters of 3 M and 10.5M of acetic acid aqueous solution showed that the aqueous solution of acetic acid can promote crystallinity. The 3 M solution showed the best performance compared to the 10.5 M solution, so the volume of this solution was altered in the amounts of 25, 50, 100, and 150 microliters, and at 100 microliters the best peak near 8.4 was observed. By changing the solvent mix to (DCB/BOH, 1:1) with 3 M acetic acid (100 microliters), a crystalline structure was observed, but its quality was lower compared to the optimal amount. As a result, SQCOF can be synthesized under optimum conditions (0.1 ml of AcOH 3M, 120 °C, 72h, and 1 ml of the mixture is equal to 1,4-dioxane and mesitylene solvents) with a satisfying crystallin PXRD pattern.

To explain the role of the added aqueous acid, it can be said that the mixture of water and protons can help the reversible bonds of squaranine formed under kinetic conditions in an irregular and amorphous manner [21]. Therefore, the presence of this aqueous acid helps to remove the framework errors and approach the crystal structure (Scheme 2).
3.2. Characterization:

SQCOF was synthesized by condensation between squaric acid and TAPP under solvothermal conditions. The reported simulated powder x-ray diffraction (PXRD) pattern of SQCOF illustrates different peaks at 7.85, 9.58, 15.90, 21.87, 22.42, 23.33, and 24.02 degrees [25]. In the experimental PXRD pattern of SQCOF, a sharp peak near 8.4 degrees (Figure 2) can be related to (200) Miller indices that were closely matched with the reported simulation (7.85) [25]. This peak indicated that the SQCOF has an excellent and acceptable crystallinity. The appearance and intensity of this peak were considered as the main criteria in the performed optimizations. Other peaks near 10.56, 11.48, 17.81, 18.02, 20.70, and 24.09 are closely matched by the reported simulated PXRD pattern [25] (Figure 2). As a result, it can be said that adding aqueous acetic acid as an auxiliary catalyst and modifying the synthesis method significantly contributes to the formation of the crystalline framework.

Also, SQCOF was characterized by FT-IR spectra (Figure S1). The C=C bond in squaranine structure is visible near 1595 cm\(^{-1}\) and sharp peaks near 1704 and 1793 cm\(^{-1}\) can be related to stretching bonds of carbonyl groups. The related peaks of N-H and O-H appeared near 2558 and 2924 cm\(^{-1}\), respectively. Other fingerprints are indicated in Figure S1.

Flower-shaped and plate-like morphology is visible in field emission scanning electron microscopy (FE-SEM) images in Figure 3 that can arise from crystalline layer packing. Energy-dispersive X-ray spectroscopy (EDS) shows the presence of carbon, nitrogen, and oxygen atoms in the SQCOF framework (Figure S2) and the map images prove the dispersion of these elements very well (Figure 4). Also, transmission electron microscopy (TEM) images illustrated that regular packing of layer and square frameworks is obtained (Figure 5).

Chemical stability of SQCOF was investigated in organic solvents such as DMF, acetonitrile, and harsh conditions e.g., boiling water, NaOH (6M), and HCl (6M). The PXRD pattern of SQCOF in (Figure S3) remained without any changes after 24h. The specific surface area calculated by BET analysis (Figure S4-A). The value of the specific surface is equal to 36 m\(^2\).g\(^{-1}\). Although this value was not satisfactory, it was close to the reported values (68 and 90 m\(^2\).g\(^{-1}\)). The pore size distribution graph indicated that most pores have a size of 1.66 nm (Figure S4-B). Solid-state UV spectra in Figure S5 of SQCOF verified a good resonance and conjugation in the framework.

4. Application of SQCOF as a catalyst

4.1. Reaction time and amount of catalyst optimizing

to investigate the effect of using SQCOF as a heterogeneous catalyst, the reaction between aniline and acetylacetone was considered as a model reaction. Effective parameters such as time of grinding and the amount of needed catalyst were studied. Figure 6 shows the effect of the grinding time. The efficiency of the reaction was improved by increasing of grinding time and SQCOF showed the best performance at 15 minutes.
To achieve the minimum consumption of SQCOF, five amounts of catalyst were investigated, and increasing the amount to 7 mg was not effective (Figure 7).

4.2. Effect of other catalysts

Figure 8 illustrates a comparison between SQCOF and Lewis acid catalysts such as FeCl$_3$, SnCl$_2$, CeCl$_3$·7H$_2$O, BiCl$_3$, AlCl$_3$·7H$_2$O, Bi(NO$_3$)$_3$, and P-toluene sulfonic acid (P-TSA) as a Bronsted acid. Many of these catalysts like SnCl$_2$, P-toluene sulfonic acid, and CeCl$_3$·7H$_2$O showed good performance and efficiency, but the inability to separate them from the reaction medium, the inability to reuse them, and the presence of toxic metals are among their disadvantages, and challenges.

4.3. Side reactions investigations

Model-SQ was synthesized for two targets. First, Model-SQ was investigated as a catalyst linker that shows a catalyzing effect but could not be separated (Figure 8). Second, to ensure that the amines and acetylacetone (as raw materials) don’t react with amines and carbonyl units of SQCOF. So, the mixtures of Model-SQ with aniline and acetylacetone were ground separately for 60 minutes and the reactions were tracked by TLC, which did not achieve any progress in the reactions (Scheme 4).

4.4. Derivatization of enaminones

To investigate the electronic effect of the substituents, many different enaminones were synthesized from different amines with donor and acceptor electron groups (Table 1). Turnover frequency (TOF) as a key factor in catalyzing performance was calculated and SQCOF shows a good performance with high TOF as a heterogenous catalyst (Table 1).

4.5. Reusability test

Reusability is a key factor in making a logical balance between economics and application. So, SQCOF was separated and washed with DCM and methanol after the model reaction and dried under vacuum, and then utilized in the next runs. SQCOF was utilizable in 7 runs with high efficiency (Figure 9).

4.6. Proposed mechanism

In the proposed mechanism, SQCOF can activate carbonyl compounds by proton, and primary amine can attack the carbonyl. The elimination of water and hydrogen shift leads to the production of enaminones (Scheme 6).

5. Conclusion

In conclusion, we investigated the effect of using aqueous acetic acid as a co-catalyst in the synthesis of SQCOF and its influence on promoting crystallinity and shorting reaction time. In this modified synthesis method, key parameters such as volume and concentration of acetic acid were optimized and the
qualification of the crystalline structure was tracked by PXRD. Then, SQCOF was utilized as a metal-free, heterogenous, and high-performance catalyst in the synthesis of enaminones under green conditions e.g., solvent-free, grinding, and ambient temperature. SQCOF shows excellent recyclable ability (7 runs) and high TOF (up to 1283 h⁻¹).

Declarations

Credit authorship contribution statement

M. Sadegh Ramezani: conceptualization, investigation, data curation, supervision, project administration, and writing.

Sadegh Safaei: investigation, writing – review and editing, data curation.

Zahra Goodarzi: investigation and data curation.

Mahsa Moradi: investigation and data curation.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at...

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Table

Table 1 is available in the Supplementary Files section

Schemes

Schemes 1-6 are available in the Supplementary Files section.

Figures
Figure 1

PXRD pattern of SOQOF under different conditions.
Figure 2

PXRD pattern of SQCOF

Figure 3
FE-SEM images of SQCOF in different resolutions.

Figure 4

Mapping images of SQCOF.
Figure 5

Transmission electron microscopy (TEM) images of SQCOF.
Figure 6

time optimization of model reaction.
Figure 7

Optimization amount of SQCOF.
Figure 8

Comparison of the catalytic performance of SQCOF with other conventional and classical catalysts.
Figure 9

Reusability test of SQCOF.

Supplementary Files

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