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Co-immobilization of Laccase and TEMPO onto Glycidyloxypropyl Functionalized Fibrous Phosphosilicate Nanoparticles for Fixing CO_2 into β-Oxopropylcarbamatesin

Liqun Fan[1] · Jinhu Wang[1] · Xianman Zhang[1] · Seyed Mohsen Sadeghzadeh[2,3] · Rahele Zhiani[2,3] · Mina Shahroudi[2,3] · Fatemeh Amarloo[2,3]

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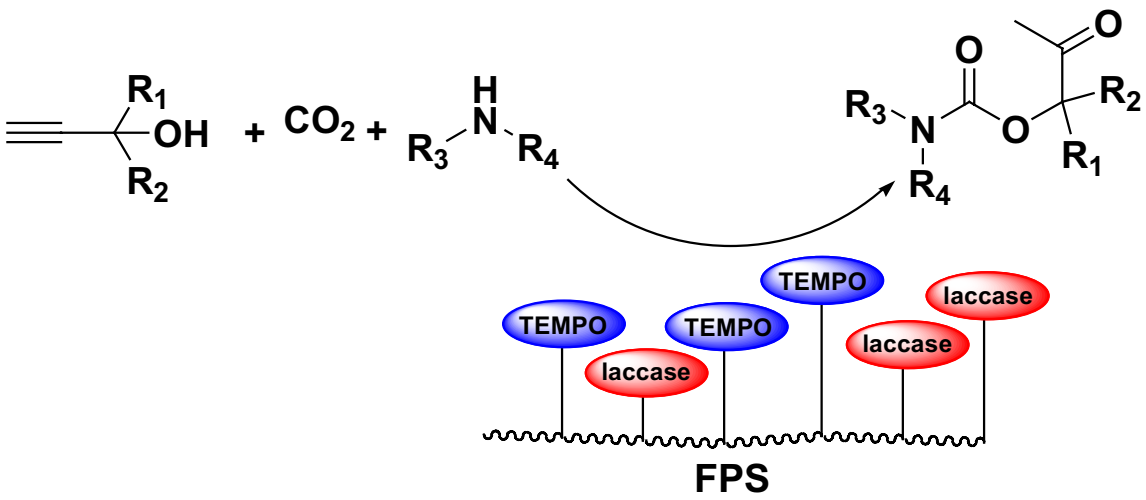
Abstract

TEMPO or Anchoring 2,2,6,6-tetra-methylpiperidine-1oxyl radical into the nanospaces a fibre of phosphosilicate with laccase compound causes an unheard potent to be producing which called bifunctional nanocatalyst (TEMPO@FPS-laccase). TEMPO@FPS-laccase indicated proper catalytic activity for synthesis of β-oxopropylcarbamates in aqueous medium without any pollutants through a multi component coupling of CO_2, amines and propargyl alcohols in moderate condition. Free laccases may not be recovered but can be easily disabled in different environmental conditions. Enzyme immobilization is known as an expanding way to enhance resistor to extreme conditions and stability as well as recycled of laccase.

Graphic Abstract



Keywords Nanocatalyst · Green chemistry · Kinetic · One-pot synthesis · Nanoparticle · Laccase

✉ Jinhu Wang
wangjinhu@uzz.edu.cn

✉ Seyed Mohsen Sadeghzadeh
seyedmohsen.sadeghzadeh@gmail.com

[1] College of Chemistry, Chemical Engineering and Materials Science, Zaozhuang University, Zaozhuang 277160, Shandong, China

[2] Young Researchers and Elite Club, Neyshabur Branch, Islamic Azad University, Neyshabur, P.O. Box 97175-613, Iran

[3] New Materials Technology and Processing Research Center, Department of Chemistry, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran

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1 Introduction

In the recent years, many studies have focused on the chemical fixation of CO_2 due to its low toxicity, cheap, unflamable, ubiquitous and reproducible attributes, that shows great facilities for the making of C–N and C–C bonds in organic production. These properties of CO_2 may be ascribed to its kinetic inertness and great stability in term of thermodynamic properties. Recently, significant approach has been obtained in this subject. Using CO_2 to produce different organic compound, like amides, esters, alcohols, carbonates and carboxylic acids as well as carbamates. It has been favored with different efficient catalytic approaches. Considerable progress has been built, and several approaches have been developing in the case of the reaction of CO_2 to products like cyclic carbonates and urethanes as well as salicylic acid and so on. One of these composite, carbamates are one of important diverse composites. Thus, utilizing carbon dioxide to synthesis an eco-friendly approach that could efficiently admit carbamates is attractive [1–4]. Among them, carbamates like β-Oxopropylcarbamates have been vastly utilized in agronomy, organic production, and pharmaceutics. Most newly, for production of boxopropylcarbamates were applied from CO_2, secondary amines and propargylic alcohols. In addition, different catalytic approaches like Ruthenium [5, 6], Fe [7], Cu [8, 9], Ag [10], and bicyclic guanidine [11] have been expanded to the multicomponent reaction. Cu, and Ag have been illustrated to be the most impressive catalysts to this reaction. Silver compounds have been showed to be the huge transition metal catalysts with particular selectivity, and they have consider able benefits over other catalysts.

Laccase can be obtained from many sources such as plants, fungi and insects. Laccase is a multicopper oxidase [12]. In the catalytic center of laccase, four copper atoms exist. It catalyses the oxidation of polyamines, polyphenols, benzenethiols and phenols by and reducing oxygen to H_2O [13–15]. In the recent years, they have attracted great attention and has been utilized in several usages, like production of the biofuel, pulp bleaching, bioremediation, and organic synthesis [16, 17]. However, it is hard to obtain free Laccasses and their efficiency in the environment of reaction is severely reduced that decrease their application in the industry.

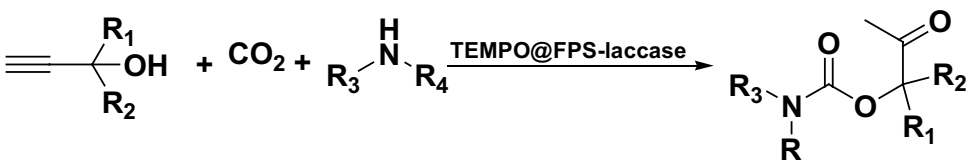
Various scholars have investigated the application of immobilized laccase in the production of organic materials, nevertheless, some laccase-catalysed reactions inevitably require the use of intermediate reagents with high costs, such as 2,2,6,6-tetramethyl-1-piperidinyloxy, creating recycling of both highly favourable enzyme and mediator, particularly for large-scale reactions [18]. Co-immobilization of a laccase or a mediator in materials that have some porosity should hence be proper, because each cavity of the support will have deferent active species [19].

Inspired by the high accessibility and low diffusion limitations of fibrous silica nanoparticles (KCC-1), fibrous phosphosilicate (FPS) was engineered using a microemulsion system [20, 21]. In the present study, an approach for the making of an impressive bifunctional hybrid catalyst through co-immobilization of TEMPO as well as laccase in the same cavities into fibres of FPS and utilized to the one-pot production of β-oxopropylcarbamates via the three-component reaction of propargylic alcohols and amines and CO_2 at moderate conditions. Exclusively, this catalytic apparatus might be quickly recycled about ten times by the lowermost catalyst loading ever reported. These great catalytic performances are ascribed to the usage of the enzyme that might do as the dual activators to both substrates and CO_2 (Scheme 1).

2 Experimental Section

2.1 Materials and Methods

All the chemical substances that were utilized in the present paper had high purity and were purchased from Fluka and Merck. Melting points of materials were obtained in open capillaries by taking advantage of an Electrothermal 9100 system. For all the purchased powders, FTIR spectra were mapped on a spectrometer of VERTEX 70 with the mode of transmission in spectroscopic grade KBr spherical pellets. The size and structure of nano particles was considered utilizing a microscope (Philips CM10 transmission electron that activated at 100 kV). Powder X-ray diffraction information were used by Bruker D8 Advance model and considering Cu ka radiation. The thermogravimetric analysis (TGA) was done on a NETZSCH STA449F3 under a constant heating rate of 10 °C min^{-1} and in the present of inert gas (nitrogen). Elemental analyses for atoms N, H and C were doneutilizing a Heraeus CHN–O-Rapid analyser. The purity definition of the products as well as reaction monitoring were carried out using TLC on



Scheme 1 Synthesis of β-oxopropylcarbamates in the presence of TEMPO@FPS-laccase NPs

silica gel polygram SILG/UV 254 plates. Mass spectra were obtained on Shimadzu GCMS-QP5050 Mass Spectrometer.

2.2 General Procedure for the Preparation of FPS

In a stirred solution with a specific volume (1.5 mL) of 1-pentanol and 30 mL of cyclohexane and, 3.7 g of tripolyphosphate as well as 2.0 g of tetraethyl orthosilicate (TEOS) were dissolved. A solution contained of 1 g of CPB and also 0.5 g of urea in 30 mL of water was enhanced to the introduced mixture. The produced mixture was then stirred, continually, for 2700 s at r.t. and after that putted into a reactor and heated at a temperature of 120 °C for 5 h. FPS was isolated for energy saving by centrifugation and washed utilizing deionized water and acetone as well as dried by a drying oven.

2.3 General Procedure for the Preparation of FPS/GMSI NPs

Twenty milliliter of THF was added to 200 mg of FPS. Then, 0.002 mol of NaH was diffused by ultrasonication. 0.022 mol of (3-glycidyloxypropyl)trimethoxysilane was added in r.t. and stirred for 16 h under a constant temperature of 50 °C. The product was washed by deionized water and an alcohol, then under vacuum dried for 3 h at a temperature of 50 °C.

2.4 General Procedure for the Preparation of TEMPO@FPS-laccase NPs

Some FPS, about 100 mg, activated by glycidyloxypropyl was released in 10 mL of acetate buffer (0.1 M and pH 4.5) comprising a constant amount of 4-hydroxy-TEMPO and laccase. The suspension was shaken under speed of 120 rpm for a few hours to produce nanoparticles containing TEMPO and co-immobilized laccase. By using acetate buffer, the resultant nanoparticles were washed several times and stored under a temperature of 4 °C.

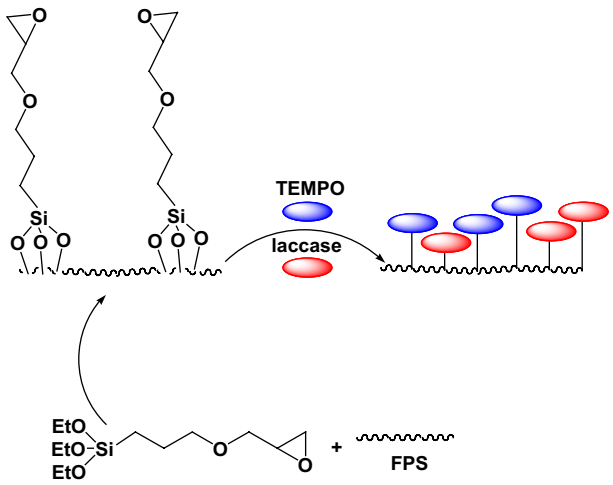
2.5 General Procedure for Catalytic Synthesis of β-Oxopropylcarbamates

Catalyst by about 5 mg, propargylic alcohols 4.95 mmol in water 0.5–1 mL and secondary amines by around 5 mmol were mixed with a Schlenk tube that equipped to a stir bar. After that the apparatus was clean with carbon dioxide for more than two times, the blend was stirred under the temperature of 50 °C and pressure of 1.5 bar for carbon dioxide for the desired time. When the considered reaction finished, the mixture was adapted by diethyl ether (3–15 mL). The upper layers were gathered and dried by vacuuming to obtain the crude yields that might be purified using more column chromatography onto silica gel by petroleum ether/ethyl acetate (100:1–20:1).

3 Results and Discussion

In the present work, FPS solution was produced with regards to reported methods and then became applicable by using (3-glycidyloxypropyl)trimethoxysilane, followed by reductive amination to make the corresponding co-immobilized TEMPO as well as enzyme. This process can be observed in Scheme 2.

The morphology and the physical structure of TEMPO@FPS-laccase NPs and FPS were analysed with FESEM and TEM analyses (Fig. 1). As seen in Fig. 1a and c, the FPS solution sample includes of wall-like domains with stable sizes of wall. Scrutiny of TEM and FESEM scheme indicated that the TEMPO@FPS-laccase is consist of dendrimeric fibers with thicknesses of 8–10 nm ordered in three dimensions to create walls, which can allow straight forward access to the high level available. From FESEM and TEM analyses of TEMPO@FPS-laccase NPs, it can be seen that this solution is not change after changing the morphology of NPs (Fig. 1b and d). Figure 2 demonstrates TGA analysis of TEMPO@FPS-laccase NPs. The deletion of the solvent of chemisorbed and physisorbed on the surface of the TEMPO@FPS-laccase material leading the weight loss. In addition, weight loss in range of 250–450 °C is almost 26.5 wt%, that is relevant to the organic group derivatives. Reducing the weight at this range of temperature can be rationalized using oxidation of TEMPO and laccase by about 180–350 °C. In fact, the residual mass after the decomposition of TEMPO@FPS-laccase NPs is because of exiting the FPS NPs.



Scheme 2 The process of co-immobilization of laccase and TEMPO onto glycidyloxypropyl-functionalized FPS nanoparticles

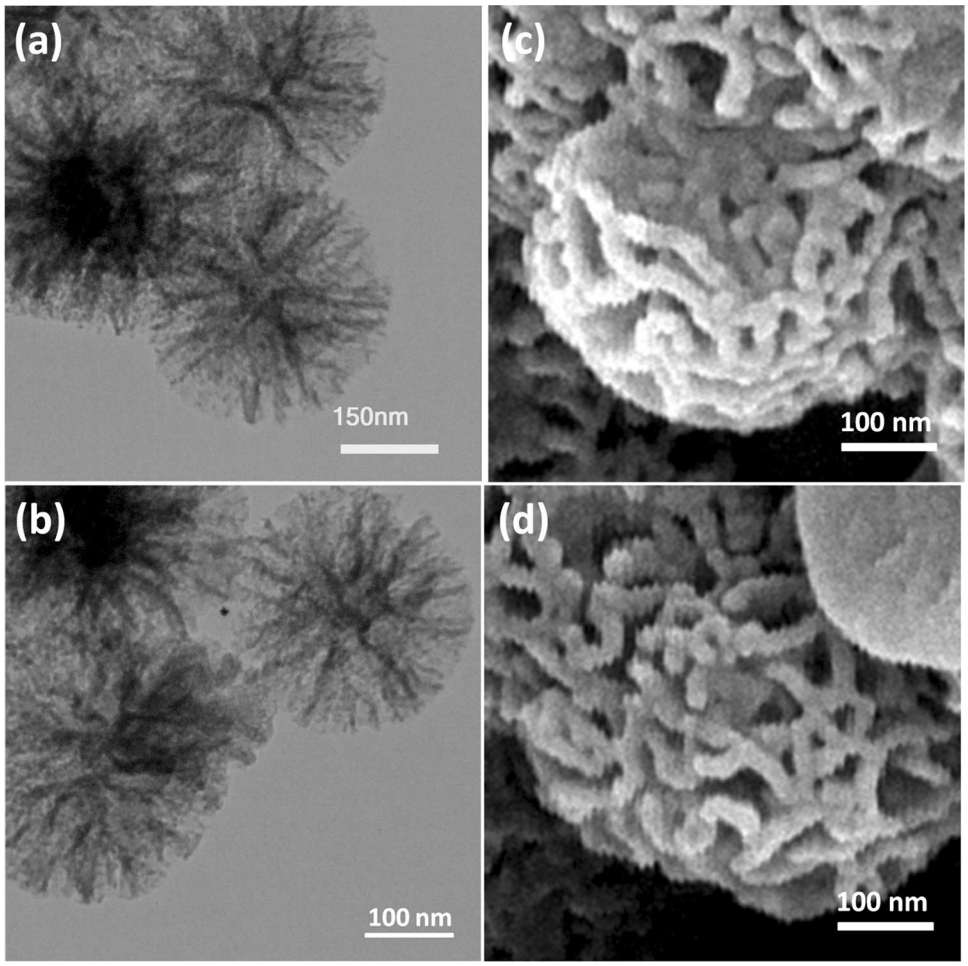


Fig. 1 TEM images of FPS NPs (**a**); TEMPO@FPS-laccase NPs (**b**); FESEM images of FPS NPs (**c**); and TEMPO@FPS-laccase NPs (**d**)

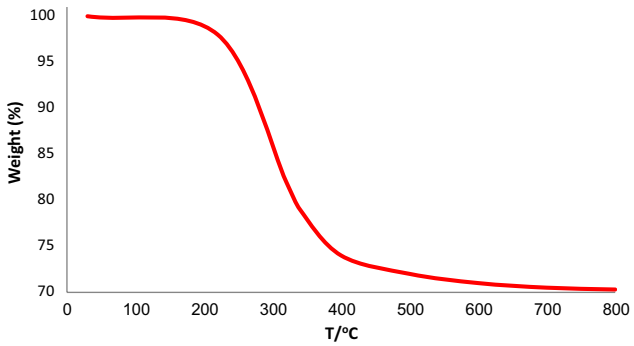


Fig. 2 TGA diagram of TEMPO@FPS-laccase NPs

Figure 3 shows the XRD pattern of FPS and TEMPO@FPS-laccase NPs. It displays a number of crystalline peaks, firm with a same reports (Fig. 3a). Figure 3b indicates a common XRD pattern of the TEMPO@FPS-laccase NPs. There was no variation. The roughness of TEMPO@FPS-laccase NPs surface was determined by atomic force microscopy analysis (AFM). Figure 4 shows the topographic images of it. As seen in Fig. 4, the greater height region indicated using the brighter yellowish white color increased with reducing T/W, offering the enhance in the catalyst surface roughness.

FTIR spectra indicated the existence of surface hydroxyl and silanols as well as phosphate groups. Figure 4 showed (a): FPS, (b): amino functionalized FPS nanoparticles. The pure FPS indicated a common broad peak by about 3399 cm^{-1} affiliated with the existence of hydroxyl groups. As seen, the intensity of this peak enhances that could be because of the existence of immobilized phosphate group on the structure of the FPS. The FPS substance sindicated additional peak about 1483 cm^{-1} that is attributed to the phosphate moiety achieving from TPP [22]. The basic peak in the spectrum of FPS is the extra peak emerged at 1232 cm^{-1}, that can be related to the –P=O stretching vibration showing the existence of phosphate group [23, 24]. The band around 963 cm^{-1} and the shoulder around 1108 cm^{-1} are because of exiting the TO and LO modes of asymmetric stretching of Si–O–P bonds [25, 26]. The band at around 724 as well as 795 cm^{-1} were related to the asymmetric expanding of the bridging oxygen atoms to a phosphor atom [27]. As seen in Fig. 5a, these peaks offered proper reaction between both

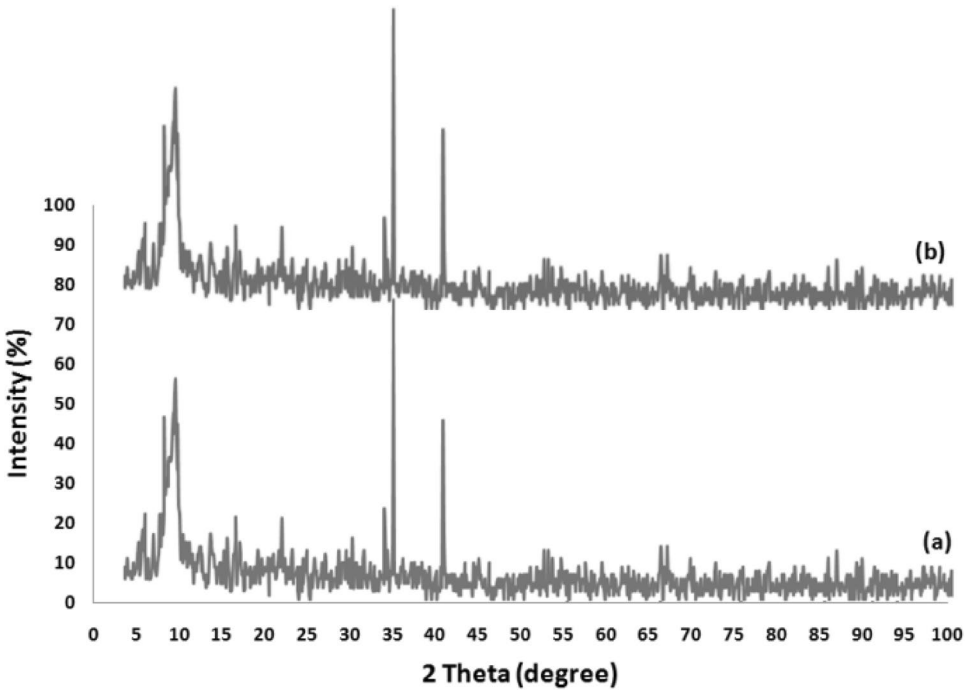


Fig. 3 XRD analysis of **a** FPS NPs; **b** TEMPO@FPS-laccase NPs

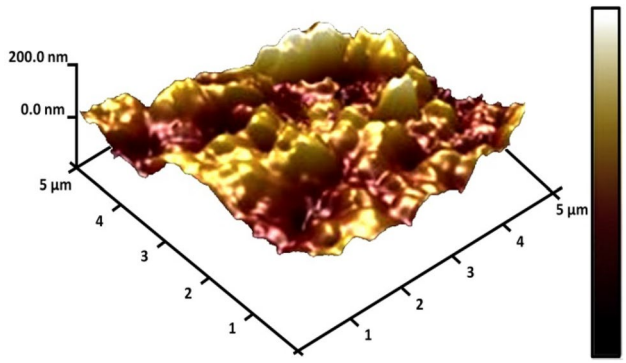


Fig. 4 Three-dimensional of AFM images of TEMPO@FPS-laccase NPs

the TEOS and the TPP. These obviously demonstrate the grafting of GMSI onto the FPS surface. The GMSI-FPS composite indicates bands at about 1091 and 793 as well as 462 cm^{-1}. A strong and broad absorption band at around 3000–3550 cm^{-1} is associated to the -OH and -NH stretching vibrancies. Figure 5b indicates that peak emerged at around 2930 cm^{-1} are because of the stretching of the C–H aliphatic group.

The analysis of Nitrogen physisorption indicated that the specific surface of BET area of FPS as well as TEMPO@FPS-laccase were 679, and 378 m^2/g. The decrease surface area of TEMPO@FPS-laccase in comparison with FPS can be due to the specifying TEMPO in the FPS. In addition, the decrease of surface area was clearer in TEMPO@FPS-laccase NPs due to low bicontinuous concentric TEMPO and also laccase morphology of the nanocatalyst. The nitrogen adsorption–desorption isotherms of FPS supported catalysts can be seen in Fig. 6. The FPS indicated a type IV isotherm, with a H1-type hysteresis loop, proposing the existence of mesopores. The related pore size section predicted by the desorption branch of the nitrogen isotherm by the BJH procedure displayed a narrow pore measure repartition peaked at 9 nm (Table 1). The large mesopore size of FPS with high capacity may load TEMPO and laccase which have comparative large molecular size.

We began investigation by the synthesis of β-oxopropylcarbamate as model substrates in existence of TEMPO@FPS-laccase NPs by 5 mg that is a nanocatalyst substance. At the beginning, we examined the influence of various solvents on final product. Table 2 shows the results of our investigation. Trace amount of β-oxopropylcarbamate was obtained for n-Hexane, Toluene and Cyclohexane (refer to Table 2, Entries 15–17). It is determined that the reaction performed proper in $CHCl_3$, i-PrOH CH_2Cl_2, CH_3CN, EtOH, MeOH and CCl_4, (Table 2, Entries 1–7). The best product (yield 97%) was obtained by adding water as the reaction environment for 12 h at a temperature of 60 °C (Table 2, Entry 14). According to the obtained results, the water is proper solvent due to its eco-friendly property synthesis of β-oxopropylcarbamate. As seen in Table 2 (Entry 20), the minimum essential temperature to carry out the reaction was studied. After investigating various temperatures, it was determined that temperature of 50 °C is the best temperature for this reaction. The temperature more than 50 °C did not

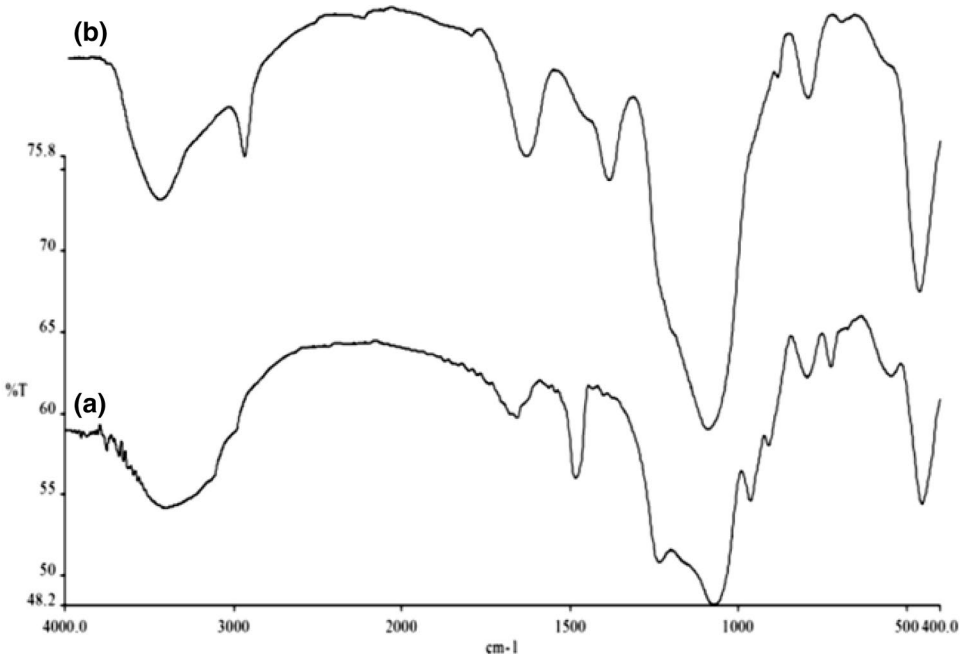


Fig. 5 FTIR spectra of **a** FPS NPs, and **b** GMSI-FPS NPs

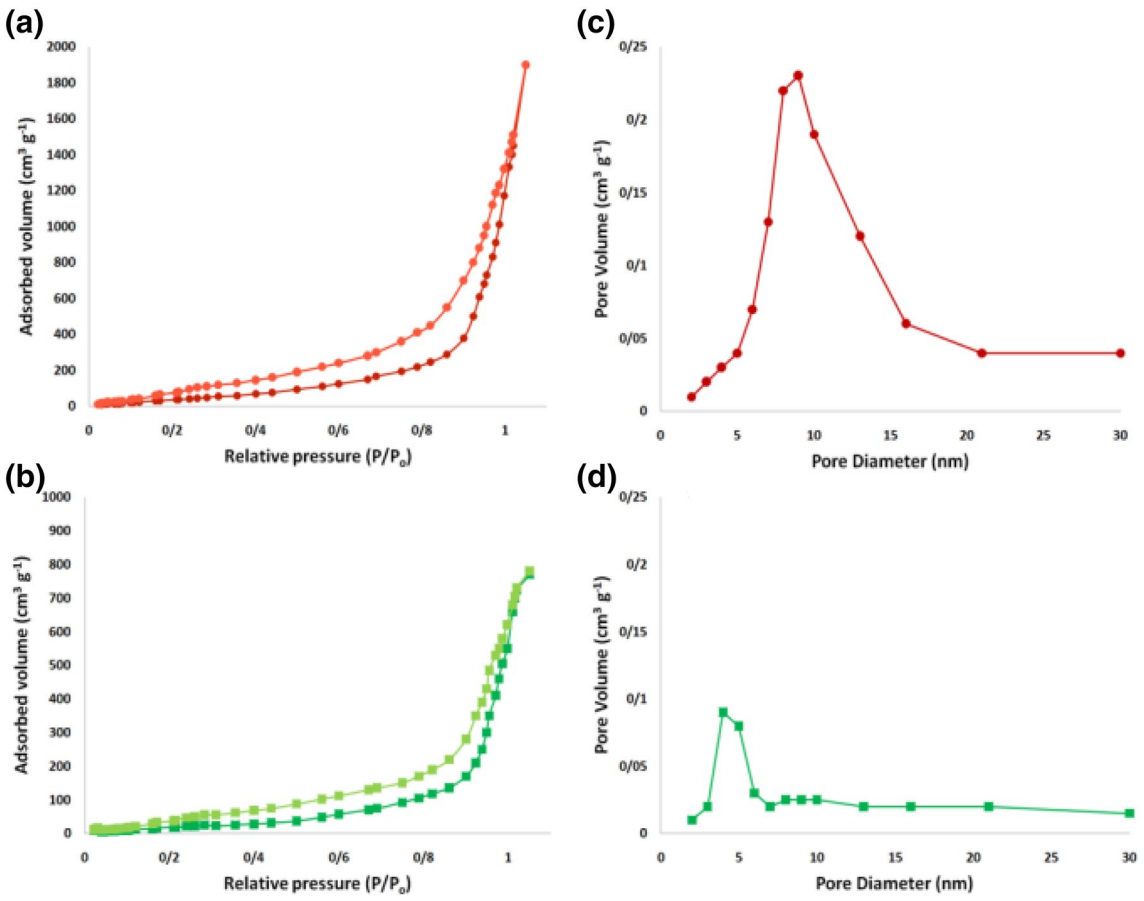


Fig. 6 Adsorption–Desorption isotherms of the FPS NPs (**a**); TEMPO@FPS-laccase NPs (**b**); and BJH pore size distributions of the FPS NPs (**c**); TEMPO@FPS-laccase NPs (**d**)

Table 1 Structural parameters of FPS, and TEMPO@FPS-laccase NPs

Catalysts	S_{BET} ($m^2\ g^{-1}$)	V_a ($cm^3\ g^{-1}$)	D_{BJH} (nm)
FPS	679	3.3	9
TEMPO@FPS-laccase	378	2.1	4

Table 2 Synthesis of β-oxopropylcarbamate by TEMPO@FPS-laccase NPs in different solvents, temperature, amount catalyst, and time

Entry	Solvent	Temperature (°C)	Catalyst (mg)	Time (h)	Yield (%)[a]
1	EtOH	60	7	12	23
2	MeOH	60	7	12	34
3	i-PrOH	60	7	12	31
4	CH_2Cl_2	60	7	12	31
5	CH_3CN	60	7	12	28
6	$CHCl_3$	60	7	12	38
7	CCl_4	60	7	12	36
8	DMF	60	7	12	28
9	DMA	60	7	12	82
10	1,4-Dioxane	60	7	12	26
11	EtOAc	60	7	12	53
12	THF	60	7	12	76
13	DMSO	60	7	12	82
14	H_2O	60	7	12	97
15	Toluene	60	7	12	7
16	*n*-Hexane	60	7	12	11
17	Cyclohexane	60	7	12	–
18	Anisole	60	7	12	16
19	Solvent-free	60	7	12	–
20	H_2O	50	7	12	97
21	H_2O	40	7	12	85
22	H_2O	50	5	12	97
23	H_2O	50	3	12	63
24	H_2O	50	1	12	21
25	H_2O	50	–	12	–
26	H_2O	50	5	10	97
27	H_2O	50	5	8	85

[a]Isolated yield

enhance yield. Another parameter which should be tested for the introduced reaction is amount of TEMPO@FPS-laccase NPs. The reaction was done for 12 h and under temperature of 50 °C, in the existence catalyst (1 mg, 3 mg, 5 mg, and 7 mg). As seen in Table 2 (Entry 25), without using a catalyst, the reaction failed to yield the β-oxopropylcarbamate. As predicted, selecting the TEMPO@FPS-laccase NPs as catalyst made a distinct change in the product amount. The reaction which using 1 mg catalyst made 21% yield and 63% product was obtained for that spreading about 3 mg catalyst after 12 h persistence. Increasing the catalyst amount to 5 mg enhanced the product of β-oxopropylcarbamate to 97%. Adding more than 5 mg of TEMPO@FPS-laccase NPs is not proper to the final yield amount (Table 2, Entry 22). Entry 26 and 27 showed the influences of time. Product yield enhanced by increasing the time from 8 to 10 h. More time to 10 h did not affect the final yield.

In addition, to enhance production of β-oxopropylcarbamate, carbon dioxide pressure was studied. The proper pressure of CO_2 for yielding the best production of TEMPO@FPS-laccase NPs would be specified whereas the kinetics of the mass transfer reactions might be changed using the diffusion and the reaction between CO_2, and 2-methylbut-3-yn-2-ol, pyrrolidine. The influence of pressure was experimentally determined ranging from 0.5 to 3.5 Mpa pressure. The function of TEMPO@FPS-laccase NPs increased forcefully while the CO_2 pressure enhanced from 0.5 to 1.5 Mpa pressure, after that it supportable in the pressure ranging from 1.5 to 3.5 MPa that can be observed in Fig. 7. These contrary facts determined the requirement for an optimum pressure around 1.5 bar for the best products of β-oxopropylcarbamate.

A time period investigation for production of β-oxopropylcarbamate was performed by immobilized TEMPO and immobilized laccase at different ratios (1:1, 1:2, 1:3, 1:4, and 1:5). As seen in Fig. 8, the best proportion of catalyst was achieved at the ratio of 1:1 and after 10 h. CO_2 cannot fixing into β-oxopropylcarbamatesin using the immobilized laccase and immobilized TEMPO singly (Fig. 9). Nevertheless, it can be observed that the co-immobilized TEMPO and laccase displaying a large capacity for synthesis of β-oxopropylcarbamate, which determined a 97% product after 10 h. The obtained results also confirmed that the TEMPO and laccase were properly supporting on the FPS. This is for the fact that the immobilized laccase and immobilized TEMPO cannot oxidase benzyl alcohol,

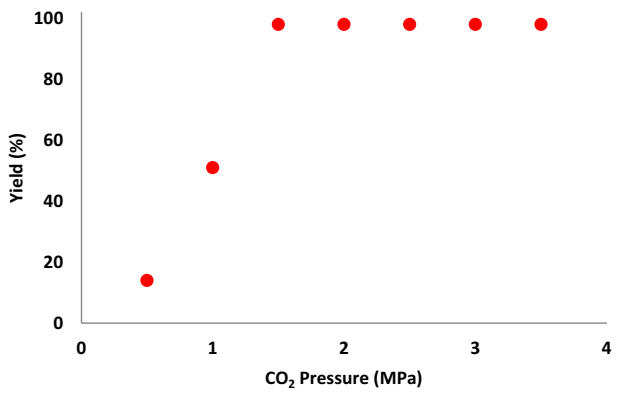


Fig. 7 The effect of CO_2 pressure on the synthesis of β-oxopropylcarbamate

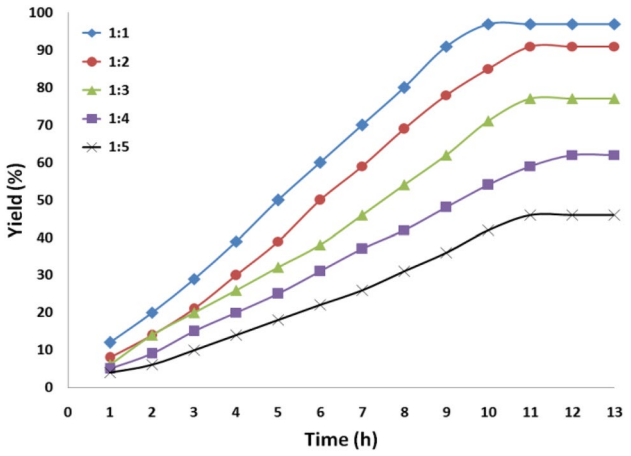


Fig. 8 Time course study of product by ratios of each component of the catalyst

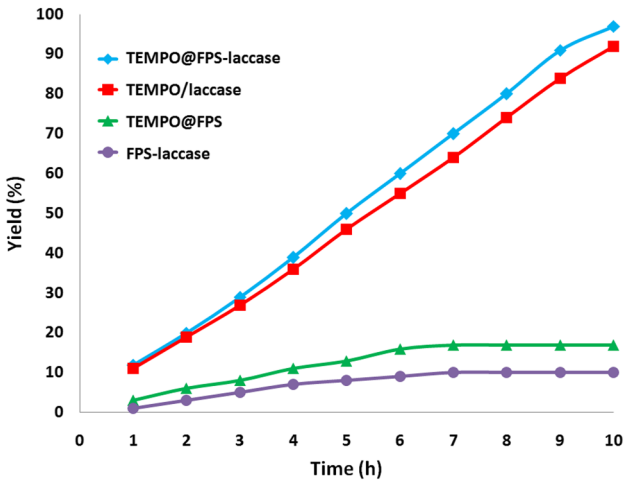
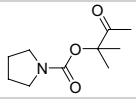
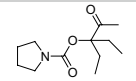
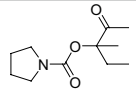
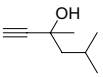
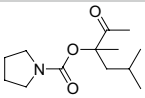
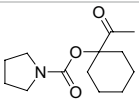
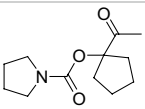
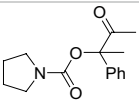
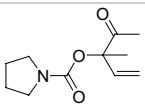
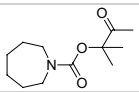
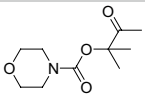
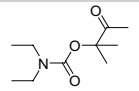
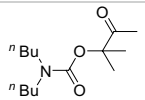


Fig. 9 Synthesis of β-oxopropylcarbamate by different FPS nanoparticles

properly, however, the of the co-immobilized laccase and TEMPO, this limitation was dominate with the adding mediator of TEMPO. Notably, there was not much difference in the reaction yields when reaction was carried out using TEMPO@FPS-laccase NPs and TEMPO/laccase catalyst, however, TEMPO/laccase is not recoverable and reusable for the next runs. These observations show that the reaction cycle is mainly catalyzed by TEMPO/laccase on the FPS nanostructure.

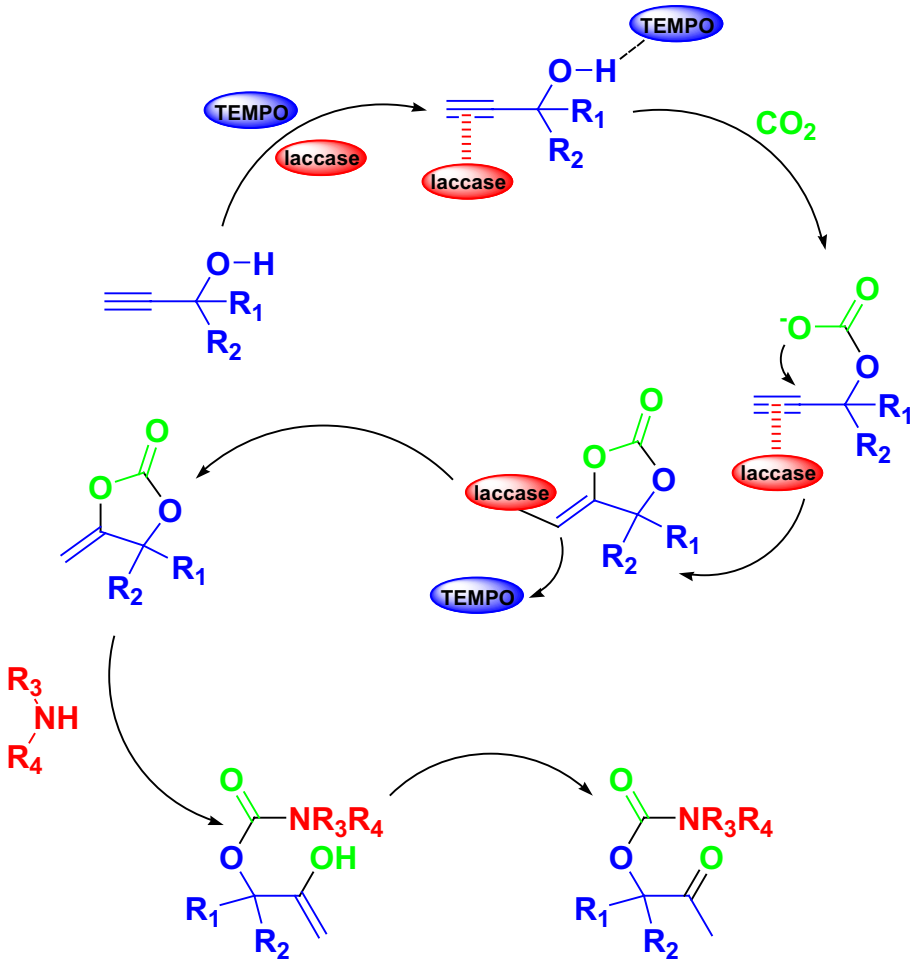
Since the conditions of reaction are improved, we then tested the substrate range using examination of the reactivity of aryl or alkyl substituents by different secondary amines. The reaction of pyrrolidine with various terminal propargylic alcohols directing alkyl substituents in the propargylic position underwent at the same condition and admitted the corresponding carbamates for yielding great

Table 3 Scope of the reaction of propargylic alcohols, secondary amines and CO_2

Entry	Amine	Alcohol	Product	Yield[a] (%)
1				97
2				82
3				94
4				80
5				56
6				77
7				65
8				86
9				91
10				95
11				92
12				88
13				65
14				74
15				48
16				59

[a]GC yields (%)

Scheme 3 Proposed catalytic mechanism of the TEMPO@FPS-laccase system



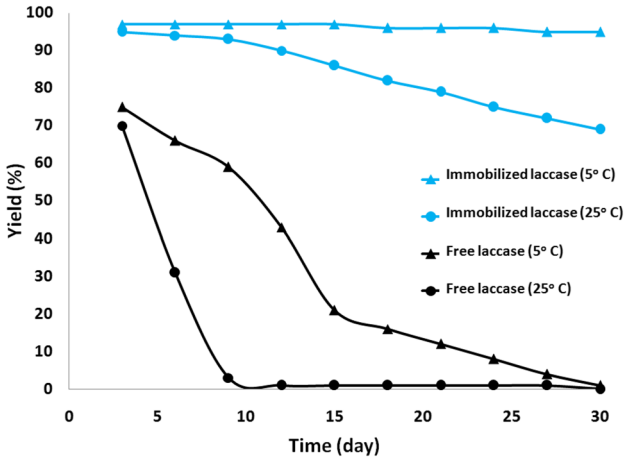


Fig. 10 Stability of the free and immobilized laccase at 5, and 25 °C for 30 days

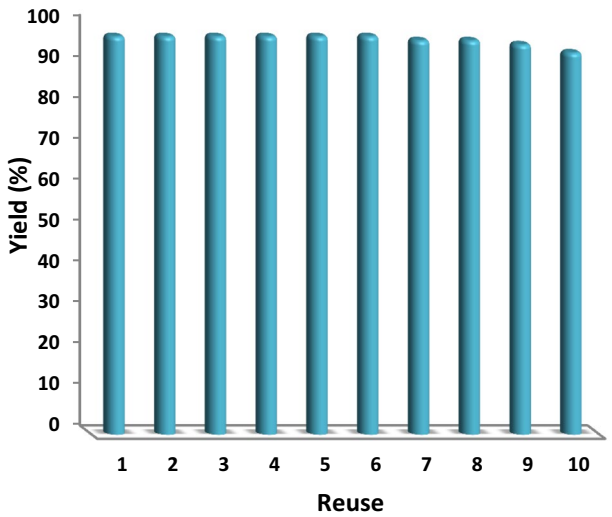


Fig. 11 The reusability of catalysts for synthesis of β-oxopropylcarbamate

yield (as observed in Table 3, Entries 1–4). Commonly, tertiary alcohols are further active compared to primary alcohols and secondary alcohols and simultaneously indicated distinct reactivity with various substituent groups.

Propargylic carbonate intermediate was quickly produced via the reaction of tertiary alcohols and carbon dioxide

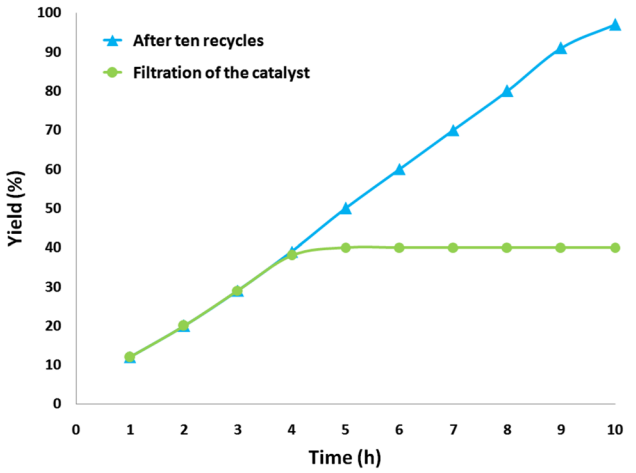


Fig. 12 Leaching test for catalyst for synthesis of β-oxopropylcarbamate

by the support of proper catalysts. Propargylic alcohols by cycloalkyl substitution done lower reactivity (can be observed in Table 3, Entries 5 and 6), and the reason would be the steric hindrance influence on the carbonate intermediate formation. In addition, other propargylic alcohols by unsaturated groups such as phenyl-substitution propose good products after adding the certain value of co-catalyst. Moreover, secondary amines represented good reactivity. Nevertheless, for the Entries 16, some lower reactivity was determined because of the steric hindrance in methyl or cyclohexyl within amines pending the nucleophilic add to a-methylene carbonate.

Relying on the above yields, a proper mechanism of TEMPO@FPS-laccase NPs is showed and it has been determined in Scheme 3. Firstly, TEMPO provide the –OH of the 2-methylbut-3-yn-2-ol and enhance the nucleophilicity of the –OH to the CO_2 that is snared and puted using the synergistic influences of TEMPO. Next, the species of laccase activates a triple bond to provide the composition of the charged oxygen by the carbon in the triple bond, causing the production of the five-membered ring. Moreover, the catalyst is dropped via five-membered ring and the main free intermediate is made. Finally, the amine offensives the carbonyl the intermediate group, followed with the tautomerism of enol to ketone as well as the production of the corresponding β-oxopropylcarbamates.

Laccase based on FPS NPs hold its activity for a thirty-day storage term under a temperature of 5 °C. Study indicated that immobilized laccase demonstrated better storage stability compared to free laccase at both selected temperatures (can be observed in Fig. 10). The free laccase was undo after few days' incubation at under temperatures of 5 and 25 °C, respectively. Some studies have presented cytotoxicity and mutagenicity in mammalian cells due to having TEMPO.

It important to know that the heterogeneous attribute of TEMPO@FPS-laccase NPs reduce its recovery property from the environment of reaction. Some power of catalyst of the recycled TEMPO@FPS-laccase NPs was investigated at the proper conditions. At the end of the reaction, TEMPO@FPS-laccase NPs was separated by taking advantage of filtration process and it's washed by alcohols and dried by using the pump. The laccase activity was reduced only about 3.9% after 10 processes and no considerable deactivation of the hybrid catalyst was seen after 6 processes (can be observed in Fig. 11). This reusability also demonstrates the high stability of this new heterogeneous system.

Eventually, we ran a leaching study to check whether this catalytic apparatus is really heterogeneous or whether this catalysis is promoted homogeneously using some of laccase and TEMPO substances leaching in the solution. The reaction was primarily mount using optimized conditions, in the existence of a ten-times reused batch of the catalyst. After a few hour ago, catalyst was deleted using hot filtration and the remained solution was stirred for six more hours. Figure 12 indicates the reaction in contrast to time with a ten-times reused catalyst batch (can be seen as a green curve) and how no more reagent use was discovered after the catalyst was deleted from the mixture (can be seen as a blue curve).

4 Conclusions

In summary, a very effective hybrid catalyst was synthesized on basis of heterogeneous substances including fundamentally various catalytic species. In this multifunctional catalyst, the laccase and mediator collaborate in an unprecedented procedure. The hybrid catalyst was well characterized, and the co-immobilization of both TEMPO and enzyme on the fibres of the FPS was observed. TEMPO@FPS-laccase indicated proper catalytic activity for production of β-oxopropylcarbamates via the three-component coupling reaction of CO_2, propargylic alcohols and amines. This green method showed some attractive environmentally friendly characteristics, like the simplicity of catalyst improvement from the reaction mixture by filtration. Heterogeneous bio-catalysts can enhance the efficiency of the catalytic apparatus in green organic production, exclusively in the presence of eco-friendly solvents.

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