RESEARCH ARTICLE

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Zn (II)-Schiff base covalently anchored to CaO@SiO₂: A hybrid nanocatalyst for green synthesis of 4H-pyrans

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Abstract

In this study, the Zn (II)-Schiff base covalently anchored onto the surface of CaO@SiO₂ nanoparticles. The structure of this hybrid nanomaterial (CaO@SiO₂-NH₂-Sal-Zn) was characterized using the analytical techniques such as Fourier transform infrared spectroscopy, field emission-scanning electron microscopy, X-ray powder diffraction, energy-dispersive X-ray spectroscopy, transmission electron microscopy, thermogravimetric analysis, and inductively coupled plasma atomic mass spectrometry. The catalytic activity of this organic-inorganic hybrid nanostructure was investigated through the green synthesis of 4H-pyran derivatives via one-pot threecomponent condensation reaction which high yields of desired products obtained under green media. The reusability experiments confirmed the stability and high performance of this hybrid nanomaterial under the reaction conditions. The retrievability of this catalyst was proved by recycling six times in reactions without significant loss in its activity. Green conditions, use of available materials, easy work-up procedure, and high yield of products, low reaction times, and simple purification are some advantages of this protocol over earlier ones.

KEYWORDS

4H-pyran, catalyst, chicken-egg shells waste, Schiff base

1 INTRODUCTION

According to the principals of green chemistry, the use of green reaction conditions including nontoxic stating materials and elimination of hazardous materials has become a huge challenge in academic and industry aspects.^[1]

Multicomponent reactions (MCRs) are a green and powerful strategy for the synthesis of different biologically active organic compounds. These reactions have many useful advantages over traditional multistep processes including short reaction times, low costs, high efficiency, atom economy, and environmentally friendliness.^[2-5] Furthermore, one of the most critical

developments in green chemistry is the widespread application of heterogeneous nanocatalysts in MCRs^[6-9] because homogeneous catalysts suffer from separation difficulty over reaction mixture. Heterogeneous catalysts compared to homogeneous ones have several advantages like milder experimental conditions, simple separation, easy recycling, and recovery of catalyst.^[10-12] Consequently, the improvement of conventional approaches in an eco-friendly manner to prepare the heterogeneous nanocatalysts is in great demand.^[13,14]

In recent years, the considerable attention to developing of green technologies in organic synthesis led to biosynthesis of nanoparticles using environmentally materials and biomolecular benign raw surface

functionalization.^[12,15] CaO obtained from waste chicken-egg shells is one of the feedstock for synthesis of green catalysts, which has several advantages including the ability to form a nanoporous structure, biodegradable, recyclable, biocompatible, high catalytic activity, and the most positive point in reducing environmental pollution associated with the wrong disposal of waste chicken-egg shells.^[16,17]

Surface-functionalized natural-based nanoparticles have emerged as suitable supports for synthesis of organic–inorganic hybrid catalysts. The surface of CaO nanoparticles can be easily functionalized with different organic groups to protect the inorganic solids core from chemical reactions and improve the behavior and overall performance. The immobilization of Schiff base onto the surface of CaO nanoparticles may produce such a hybrid nanoparticle, which can be used as a green catalyst for synthesis of several organic compounds.

Recently, the use of multicomponent reactions as a suitable method for synthesis of 4*H*-pyran motifs has also gained great attention due to their biological and pharmacological activities. These compounds perform diverse therapeutic activities, such as anti-inflammatory, spasmolytic, antimicrobial, anticoagulant, anticancer, and anti-anaphylactic properties.^[18–20]

Based on the above considerations and also due to our interests in synthesis of heterocyclic compounds,^[21–23] we wish to report an environmentally benign procedure for synthesis of some dihydropyrano[c]chromenes, dihydropyrano[3,2-c]pyrazoles and tetrahydrobenzo[b] pyrans, via one-pot three-component reactions of related materials in the presence of a novel prepared CaO@SiO₂-NH₂-Sal-Zn hybrid nanomaterial as an efficient and green catalyst (Scheme 1).

2 | EXPERIMENTAL

2.1 | General information

All reagents and solvents were purchased from Merck and Fluka companies. Nuclear magnetic resonance (NMR) spectra were recorded on а 300-MHz Brucker-Avance spectrometer using tetramethylsilane (TMS) as an internal standard. IR spectra were obtained by ALPHA-BRUKER spectrophotometer using KBr pellets. The particle size and external morphology of the nanoparticles as well as their components were assaved by field emission-scanning electron microscopy (FE-SEM) analyses. The energy-dispersive X-ray (EDX)



SCHEME 1 Synthesis of 4*H*-pyrans in the presence of CaO@SiO₂-NH₂-Sal-Zn as a catalyst

and the X-ray powder diffraction (XRD) were carried out by MIRA III and PW1730 instruments, respectively. Transmission electron microscopy (TEM) was performed using a Philips EM208S 100KV. Thermogravimetric analysis (TGA) curves were recorded using a Q600TA analyzer and inductively coupled plasma atomic mass spectrometry (ICP-MS) carried out by Agilent 7500.

2.2 | Synthesis of silica-coated CaO nanoparticles (CaO@SiO₂)

Nano-CaO particles were prepared according to the reported method in the literature from eggshells waste.^[24] Silica-coated CaO nanoparticles were prepared by the Stober method.^[22] Briefly, nano-CaO (1 g) was sonicated in a mixture of ethanol (40 ml), deionized water (6 ml), and 1.5 ml of 25 wt% concentrated aqueous ammonia for 20 min at room temperature. Then, 1.4 ml of tetraethyl orthosilicate (TEOS) was added and the resulting mixture stirred for 22 h at room temperature under N₂ atmosphere. Finally, CaO@SiO₂ core-shell nanoparticles were successively separated using a centrifuge, which washed several times by ethanol and deionized water and dried for 24 h by vacuum dryer.

2.3 | Synthesis of chloropropyl-modified silica-coated CaO nanoparticles (CaO@SiO₂-cl)

The CaO@SiO₂ (1 g) was dispersed in dry toluene (50 ml) by ultrasonic vibrations for 20 min. Then, (3-chloropropyl)trimethoxysilan (1.8 ml, 10 mmol) was added dropwise to the suspension and the mixture refluxed for 24 h under N₂ atmosphere. The resulted product was separated by centrifuge, washed several times with toluene, and dried under vacuum conditions at 80° C.

2.4 | Synthesis of triethylenetetraminefunctionalized silica-coated CaO nanoparticles (CaO@SiO₂-NH₂)

Dispersion of CaO@SiO₂-Cl (1 g) in dry toluene (50 ml) was carried out by ultrasonic waves for 30 min. Subsequently, triethylenetetramine (2.1 ml, 15 mmol) and triethylamine (0.1 ml) were added dropwise to the reaction mixture and refluxed for 24 h under N₂ atmosphere. The resulted solid product was separated from the solution using a centrifuge, washed with toluene, and finally dried at 80° C.

2.5 | Preparation of the shift base-functionalized nanoparticles (CaO@SiO_2-NH_2-Sal)

 $CaO@SiO_2-NH_2$ nanoparticles (1 g) and of salicylaldehyde (2 mmol) were dispersed in dry toluene (50 ml) by ultrasonic vibrations. The reaction mixture was refluxed for 24 h under N₂ atmosphere. The solid $CaO@SiO_2-NH_2-Sal$ was filtered, washed with toluene, and dried under vacuum at 80°C.

2.6 | Preparation of Zn (II)-decorated CaO@SiO₂-NH₂-Sal nanoparticles (CaO@SiO₂-NH₂-Sal-Zn)

A mixture of CaO@SiO₂-NH₂-Sal (0.5 g), ZnCl₂ (0.5 mmol) and ethanol (20 ml) in a dry flask was put in an ultrasonic bath for 20 min and refluxed for 24 h under N₂ atmosphere. Then, the catalyst was separated from the solution using a centrifuge, washed with ethanol, and dried in the vacuum dryer at 80°C for 24 h.

2.7 | General procedure for the synthesis of 4*H*-pyrans in the presence of the hybrid nanocatalyst (CaO@SiO₂-NH₂-Sal-Zn)

А mixture of malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol) /or 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmole) /or 5,5-dimethylcyclohexan-1,3-dione (1 mmol) and aromatic aldehyde (1 mmol) and CaO@SiO₂-NH₂-Sal-Zn (0.01 g) in a round-bottomed flask was mechanically stirred at room temperature for an appropriate time (Table 2). After completion of the reaction, which was confirmed by thinlaver chromatography (TLC), hot ethanol (10 ml) was added and stirring continued at room temperature for 10 min. The catalyst was separated easily by centrifuge and the solution cooled to room temperature to precipitate the product. The solid product was filtered and recrystallized from EtOH to obtain pure product.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of CaO@SiO₂-NH₂-Sal-Zn catalyst

Synthesis of Zn (II)-Schiff base covalently stabilized onto the surface of $CaO@SiO_2$ nanoparticles was carried out carefully as shown in Scheme 2. Firstly, the silica-coated CaO nanoparticle was prepared from clean eggshells



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SCHEME 2 The schematic pathway for preparation of CaO@SiO2-NH2-Sal-Zn

waste using our previously reported method.^[22] Subsequently, (3-chloropropyl)trimethoxysilan was reacted with silica-coated CaO to form CaO@SiO₂-Cl. CaO@SiO₂-NH₂ was prepared by the simple procedure between triethylenetetramine and CaO@SiO₂-Cl. In the next step, the reaction of salicylaldehyde with CaO@SiO₂-NH₂ afforded CaO@SiO₂-NH₂-Sal, which then converted to CaO@SiO2-NH2-Sal-Zn by treatment with ZnCl₂. The structure of CaO@SiO₂-NH₂-Sal-Zn was established by Fourier transform infrared spectroscopy (FT-IR), FE-SEM, TEM, energy-dispersive X-ray spectros-(EDS). X-ray diffraction (XRD), copy and thermogravimetry analysis (TGA), and inductively coupled plasma atomic mass spectrometry (ICP-MS) techniques.

Figure 1 shows FT-IR spectra of (a) CaO, (b) CaO@SiO₂, (c) CaO@SiO₂-Cl, (d) CaO@SiO₂-NH₂ (e) CaO@SiO₂-NH₂-Sal, and (f) CaO@SiO₂-NH₂-Sal-Zn. In Figure 1a, the strong vibration band around 529 cm^{-1} shows the characteristic adsorption of Ca-O from pure CaO.^[24] The broad absorption bands around 3400-3600 cm⁻¹ assigned to OH stretching vibration and physically adsorbed water (H₂O).^[16] The weak band at

1481 cm⁻¹ is attributed to asymmetric C-O stretching of carbonate ion. CaO@SiO2 spectrum shows distinguished vibration bands in FT-IR (Figure 1b). The peaks observed around 968, 876, and 462 cm⁻¹ are attributed to symmetric stretching, in-plane bending, and rocking mode of the Si-O-Si groups, respectively. The twisting vibration mode of adsorbed H-O-H in the silica shell is seen at 1641 cm^{-1} . The stretching vibration mode of Si-OH is apparent in the range 3200-3500 cm^{-1.[[22]]} The weak adsorption bands at 2862 and 2936 cm⁻¹ are related to the symmetric and asymmetric stretching modes of C-H bonds which indicating the definite attach of (3-chloropropyl)trimethoxysilan groups (Figure 1c). The stretching vibration of amine group in CaO@SiO₂-NH₂ is observed at 3173 and 3287 cm^{-1} (Figure 1d). The bending vibrations of N–H groups appeared at 1597 cm^{-1} , and the band at 1632 cm^{-1} proved the existence of imine group (Figure 1e). The two absorption bands around 546 and 511 cm⁻¹ indicate the existence of Zn-O and Zn-Cl vibration, respectively, which overlapped with vibration band for CaO@SiO₂ (Figure 1f).^[25,26] On the other hand, the shifting of C=N vibrational band to lower frequency (1625 cm⁻¹) in the spectrum of CaO@SiO₂-NH₂-Sal-Zn

FIGURE 1 Fourier transform infrared spectroscopy (FT-IR) spectra for (a) CaO, (b) CaO@SiO₂, (c) CaO@SiO₂-Cl, (d) CaO@SiO₂-NH₂, (e) CaO@SiO₂-NH₂-Sal, and (f) CaO@SiO₂-NH₂-Sal-Zn





FIGURE 2 Field emission-scanning electron microscopy (FE-SEM) (a) and transmission electron microscopy (TEM) (b) images of CaO@SiO₂-NH₂-Sal-Zn hybrid nanomaterials

(Figure 1f) is in support of zinc complex band formation.^[27] These spectra clearly confirm the structure of CaO@SiO₂-NH₂-Sal-Zn hybrid nanomaterials.

The FE-SEM technique and TEM were employed for studying the size and morphology of $CaO@SiO_2-NH_2-Sal-Zn$ (Figure 2). As shown in Figure 2, these nanoparticles are spherical with an average size of about 38–44 nm. The observed agglomeration in the FE-SEM images is due to high-specific surface area of nanoparticles, which led to aggregation. TEM analysis shows dark regions coated by bright outer shells, which indicates silica as a shell is successfully anchored to the CaO as a core.

The EDS analysis for CaO@SiO₂-NH₂-Sal-Zn nanomaterial is presented in Figure 3. The presence of Si, O, Ca, N, C, and Zn is clearly matched with the structure for CaO@SiO₂-NH₂-Sal-Zn nanostructure. Also, the increasing intensity of Si compared to that of Ca confirms that CaO nanoparticles were trapped by the SiO₂ shell.

The X-ray diffraction (XRD) patterns were implemented to investigate structural properties of CaO and CaO@SiO₂-NH₂-Sal-Zn (Figure 4). The crystalline structure of CaO nanoparticles caused diffraction peaks at $2\theta = 32.50^{\circ}$, 37.65° , 54.16° , 64.54° , and 67.71° which are attributed to the Miller indices (hk l) at (111), (200), (202), (311), and (222), respectively.^[24] The position and





FIGURE 3 The energy-dispersive X-ray spectroscopy (EDS) analysis of CaO@SiO2-NH2-Sal-Zn hybrid nanomaterials



FIGURE 4 The X-ray diffraction (XRD) patterns of (a) CaO nanoparticles and (b) CaO@SiO₂-NH₂-Sal-Zn hybrid nanomaterials

intensity of all peaks agree with the standard calcite CaO sample (JCPDS card no.77-9574). The broad peak around $2\theta = 18^{\circ}$ to 24° can be indexed to amorphous silica phase of CaO@SiO₂-NH₂-Sal-Zn (Figure 4b).^[28] The average size of the crystals can be estimated by the (200) XRD peak and applying Scherrer's formula ($D = 0.9\lambda/\beta \cos \theta$). In this formula, *D* denotes the average crystalline size, λ represents the wavelength (200) of the incident X-ray, β is the full width of the (200) powder peak by the radian subtended at half maximum intensity, and θ corresponds to the Bragg diffraction angle of the (200) peak in degrees. The peak at $2\theta = 37.65^{\circ}$ (200) is selected to calculate the crystallite size. The average crystallite size of CaO@SiO₂-NH₂-Sal-Zn is about 35 nm by using

Scherrer's equation, which is according to the particle sizes obtained from FE-SEM data.

TGA and derivative thermogravimetry (DTG) of the CaO@SiO₂-NH₂-Sal-Zn nanoparticles are presented in Figure 5. The thermal decomposition of this nanostructure shows two weight loss steps. The first step, a weight loss of about 6% from room temperature to nearly 150° C, is due to the removal of organic solvents, water and surface hydroxyl groups (Figure 5). The second step weight loss (27.5%), beyond 150° C to nearly 649° C, is attributed to the decomposition of the organic tags. Finally, after 649° C, decomposition of calcium carbonate to CaO and CO₂ is observed. Based on this mass loss, the attaching of NH₂-Sal-Zn on the surface of CaO@SiO₂ is confirmed.

FIGURE 5 Thermogravimetic analysis (TGA/DTG) of CaO@SiO₂-NH₂-Sal-Zn



TABLE 1 The optimization of reaction conditions for synthesis of 2-amino-4-(4-nitrophenyl)-5-oxo-4H,5H-pyrano[3, 2-c]chromene-3-carbonitrile

Entry	Catalyst (g)	Solvent	Temp (°C)	Time (min)	Yield (%) ^[a]
1	-	-	25	150	trace
2	CaO@SiO ₂ -NH ₂ -Sal-Zn)0.005)	-	25	30	88
3	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.008)	-	25	20	95
4	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	-	25	10	97
5	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	-	50	10	97
6	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	-	100	10	95
7	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.02)	-	25	15	97
8	CaO (0.01)	-	25	60	80
9	$CaO@SiO_2(0.01)$	-	25	60	82
10	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	H ₂ O	25	30	70
11	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	EtOAc	25	30	75
12	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	EtOH	25	20	92
13	CaO@SiO ₂ -NH ₂ -Sal-Zn (0.01)	CHCl ₃	25	60	72

Note: Isolated yield.

^aReaction conditions: malononitrile (1, 1 mmol), 4-nitrobenzaldehyde (2, 1 mmol) and 4-hydroxycoumarin (3, 1 mmol).

3.2 | Synthesis of 4*H*-pyrans catalyzed by CaO@SiO₂-NH₂-Sal-Zn

In order to determine the best results in terms of reaction temperature, solvent, and catalyst amount, initially, the reaction of malononitrile (1), 4-nitrobenzaldehyde (2) and 4-hydroxycoumarin (3) as a model reaction was examined for synthesis of 2-amino-4-(4-nitrophenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile **6f**.

The different solvents (EtOH, CHCl₃, EtOAc, and H₂O at room temperature) as well as solvent-free medium, temperatures, and catalyst amounts were examined on model reaction, and the results are shown in Table 1. The solvent-free medium, room temperature, and use of 10 mg of hybrid catalyst (CaO@SiO₂-NH₂-Sal-Zn) serve as the best condition with respect to the green nature and clean work-up procedure for this synthesis (Table 1, entry 4). These results encouraged us to investigate the scope of this method for synthesis of 4*H*-pyran, in the presence of various aldehydes with both electron-withdrawing and electron-releasing substituents under optimized condition. It was found that the reactions for all of the various substrates proceed efficiently to obtain the desired products in good to excellent yields in relatively short reaction

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> times and without formation of side products (Table 2). The characterization data for desired products are presented in the Supporting information.

> The comparison of the catalytic efficiency of CaO@SiO₂-NH₂-Sal-Zn in the present work with previously reported methods is shown in Table 3. The presented data confirm that the CaO@SiO₂-NH₂-Sal-Zn is a

TABLE 2	Synthesis of the 4H-pyran derivatives in	the presence of CaO@SiO ₂ -NH ₂ -Sal-Zn
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Entry	Ar/Aldehyde	Product	Time (min)	Yield (%) ^[a]	M.P (Obs.) (°C)	M.P (Lit.) (°C)
1	C ₆ H ₅	6a	30	93	267-269	271-273 ^[30]
2	2-ClC ₆ H ₄	6b	25	91	269–271	273-274 ^[30]
3	2,4-Cl ₂ C ₆ H ₃	6c	20	92	280-281	283-284 ^[30]
4	$2-NO_2C_6H_4$	6d	25	92	250-252	255-256 ^[30]
5	$3-NO_2C_6H_4$	6e	20	90	230-232	229-231 ^[29]
6	$4-NO_2C_6H_4$	6f	10	97	260-262	263-264 ^[31]
7	2-BrC ₆ H ₄	6 g	20	89	293-295	295-297 ^[32]
8	3-BrC ₆ H ₄	6 h	25	91	273–274	274–276 ^[33]
9	3-OHC ₆ H ₄	6i	30	90	258-260	262-263 ^[34]
10	3-OEt-4-OHC ₆ H ₃	6j	20	94	245-247	248-250 ^[31]
11	4-FC ₆ H ₄	6 k	25	88	246-248	250-252 ^[35]
12	2,5-(OMe) ₂ C ₆ H ₃	6 L	35	90	223-225	228-230 ^[36]
13	2-naphthaldehyde	6 m	30	92	263-264	263-265 ^[30]
14	3-phenoxybenzaldehyde	6n	25	90	138–139	-
15	C ₆ H ₅	7a	30	92	170–172	170–173 ^[37]
16	$2\text{-}ClC_6H_4$	7b	25	89	141–143	145-146 ^[18]
17	$3-ClC_6H_4$	7c	30	92	158–161	161-163 ^[38]
18	4-ClC ₆ H ₄	7d	15	95	170–172	169–171 ^[39]
19	4-FC ₆ H ₄	7e	15	89	183–186	186–187 ^[40]
20	$3-BrC_6H_4$	7f	20	93	165–167	164–167 ^[38]
21	$2,4-Cl_2C_6H_3$	7 g	15	94	185–187	188-193 ^[38]
22	3-OEt-4-OHC ₆ H ₃	7 h	20	95	187–189	186-190 ^[37]
23	2-naphthaldehyde	7i	25	90	196–197	205-207 ^[41]
24	terephthalaldehyde	7j	40	85	235-237	236-238 ^[42]
25	[1,1'-biphenyl]-4-carbaldehyde	7 k	25	93	191–193	193–194 ^[42]
26	C_6H_5	8a	30	93	225-227	228-230 ^[43]
27	$2\text{-}ClC_6H_4$	8b	25	83	216-218	217-219 ^[43]
28	$2,3-Cl_2C_6H_3$	8c	20	91	282-283	280-282 ^[44]
29	4-FC ₆ H ₄	8d	25	92	210-214	210-214 ^[22]
30	1-naphthaldehyde	8e	20	93	213-215	214-215 ^[45]
31	Pyridine-4-carbaldehyde	8f	20	95	260-262	265-266 ^[46]
32	2,2'-(butane-1,4-diylbis (oxy) dibenzaldehyde	8 g	25	95	209–211	209-211 ^[22]
33	[1,1'-biphenyl]-4-carbaldehyde	8 h	30	83	163–166	-

Note: Isolated yield.

^aReaction conditions: malononitrile (1, 1 mmol), arylaldehyde (2, 1 mmol), 4-hydroxycoumarin (3, 1 mmol) /or 3-methyl-1-phenyl-2-pyrazolin-5-one (4, 1 mmole) /or 5,5-dimethyl-cyclohexan-1,3-dione (5, 1 mmol), and catalyst (0.01 g).

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Entry	Catalyst	Condition	Time (min)	Yield (%) ^[a]	Ref.
1	Fe ₃ O ₄ @GO-naphthalene-SO ₃ H	H ₂ O/r.t	10	91	[47]
2	Hexamethylenetetramine (HMT)	EtOH/reflux	15	94	[32]
3	S-proline	H ₂ O/EtOH-reflux	360	82	[34]
4	(Diammonium hydrogen phosphate)DAHP	H ₂ O/EtOH-reflux	480	95	[34]
5	SDS (Sodium dodecyl sulfate)	$H_2O/60^\circ C$	360	96	[48]
6	[Sipim]HSO ₄	s.f/100°C	90	88	[49]
7	Ni (II)-Schiff base/SBA-15	$H_2O/70^\circ C$	10	97	[30]
8	CaO@SiO ₂ -NH ₂ -Sal-Zn	s.f/r.t	10	97	Present work

TABLE 3 The comparison of CaO@SiO₂-NH₂-Sal-Zn with other catalysts reported in the literatures for synthesis of 2-amino-4-(4-nitrophenyl)-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile

Note: Isolated yield.

^aReaction conditions: malononitrile (1, 1 mmol), 4-nitrobenzaldehyde (2, 1 mmol) and 4-hydroxycoumarin (3, 1 mmol).

comparable, suitable, and efficient catalyst for the synthesis of desired 4*H*-pyrans. The application of CaO@SiO₂-NH₂-Sal-Zn as a hybrid catalyst in solvent-free medium at room temperature led to the greener condition for this synthetic protocol. The porosity and high surface area of nanostructure (CaO@SiO₂-NH₂-Sal-Zn) and Lewis acidity of Zn ions increase the catalytic performance of the prepared hybrid nanomaterial.

The plausible mechanism for the synthesis of dihydropyrano[c]chromene derivatives **6** in the presence of CaO@SiO₂-NH₂-Sal-Zn is similar to that reported in the literature.^[29] As illustrated in Scheme 3, a Knoevenagel condensation between malononitrile and catalyst-activated aldehyde generates arvlidene malononitrile (intermediate I). The nucleophilic attack of 4-hydroxycoumarin on intermediate I, via Michael addition, affords the intermediate II. The reaction is followed by consecutive intermolecular cyclization to give the intermediate III, which gives the desired product after tautomerization (Scheme 3). Similar mechanisms for the synthesis of dihydropyrano[3,2-c]pyrazoles 7 and tetrahydrobenzo[b]pyrans 8 in the presence of CaO@SiO₂-NH₂-Sal-Zn are proposed.

3.3 | Catalyst reusability

The possibility of recycling $CaO@SiO_2-NH_2-Sal-Zn$ as a catalyst was investigated in the model reaction under the optimized conditions. Upon completion of the reaction, 10-ml hot ethanol was added and the catalyst was collected by centrifuge, washed with ethanol, dried in a vacuum oven, and reused for next reaction. The recycled catalyst can be used in the model reaction for six times without any additional treatment and significant loss of its initial catalytic activity (Figure 6). The structure



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SCHEME 3 The possible mechanism for one-pot synthesis of dihydropyrano[c]chromenes using CaO@SiO₂-NH₂-Sal-Zn as a catalyst

of fresh and reused catalyst after six runs were compared by FT-IR (Figure 7) and XRD patterns (Figure 8). The activity and structure of reused catalyst (CaO@SiO₂-NH₂-Sal-Zn) prove the high stability and recyclability of this catalyst. The exact amount of zinc loaded on CaO@SiO₂-NH₂-Sal was evaluated using the ICP/MS analysis. According to the results obtained by ICP/MS technique, the exact amount of zinc in the hybrid nanocatalyst was estimated to be 0.81 mmol g⁻¹ for fresh CaO@SiO₂-NH₂-Sal-Zn and 0.73 mmol g⁻¹ for catalyst after six runs. These results verify that the leaching of zinc in the reaction mixture is negligible, and this catalyst has good stability.



FIGURE 6 Recyclability of CaO@SiO₂-NH₂-Sal-Zn for synthesis of model reaction



FIGURE 7 Fourier transform infrared spectroscopy (FT-IR) spectra of the fresh catalyst and the six-time reused catalyst



FIGURE 8 X-ray diffraction (XRD) spectra of the fresh catalyst and the six-time reused catalyst

4 | CONCLUSION

In this work, surface-modified CaO nanoparticles (from biogenic wastes) were functionalized with the Zn (II)-

Schiff base complex. The novel Zn-complex decorated hybrid nanostructure (CaO $@SiO_2$ -NH₂-Sal-Zn) was characterized successfully using various techniques, and its catalytic activity was considered in the synthesis of

various 4*H*-pyrans. The desired products were synthesized by one-pot three-component condensation reaction under solvent-free condition. Besides, using this catalyst benefits many features including generality, synthesis of pure products in high yields, short reaction times, green nature, low-cost, simple experimental procedure, easy work-up procedures, and high recovery ability. It is noteworthy that the Zn grafting with organic functional groups on inorganic support efficiently limits Zn leaching, which permitted this hybrid nanomaterial to be reused several times with only a slight diminish in its catalytic activity.

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AUTHOR CONTRIBUTIONS

Fatemeh Sameri: Investigation; methodology. Mohammad Ali Bodaghifard: Validation. Akbar Mobinikhaledi: Project administration; supervision.

CONFLICT OF INTEREST

The authors have no any conflict of interests to declare.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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