

An efficient one-pot three-component synthesis of 7-amino -2,4-dioxo-5-aryl-1,3,4,5-tetrahydro-2*H*-pyrano[2,3-*d*] pyrimidine-6-carbonitriles catalyzed by SnO₂/SiO₂ nanocomposite

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Abstract

We have developed a $\text{SnO}_2/\text{SiO}_2$ catalyzed efficient and rapid protocol for the synthesis of pyrano[2,3-*d*]pyrimidinone derivatives by the three-component cyclocondensation of aromatic benzaldehydes, malononitrile, and barbituric acid in ethanol at room temperature. Nanocomposite $\text{SnO}_2/\text{SiO}_2$ catalytic materials were synthesized using the sol–gel method. The synthesized catalytic materials were well characterized by using a transmission electron microscope, X-ray diffraction spectroscopy, scanning electron microscopy, energy dispersive spectroscopy, Fourier transform infrared spectroscopy, temperature-programmed desorption (NH₃-TPD), and Brunauer–Emmett–Teller theory. This protocol has several advantages such as high yield, simple workup procedure, non-toxic, clean, and easy recovery and reusability of the catalytic system.

Graphic abstract

An efficient catalytic system has been developed for the synthesis of pyrano[2,3-*d*] pyrimidinone derivatives from one-pot three-component cyclocondensation of aromatic benzaldehydes, malononitrile, and barbituric acid in ethanol at room temperature using 15 wt% SnO_2/SiO_2 .



Extended author information available on the last page of the article

Keywords $SnO_2/SiO_2 \cdot Nanocomposite \cdot Sol–gel \cdot Pyrano pyrimidinones \cdot Cyclocondensation$

Introduction

A catalyst is a substance that enhances the rate of a chemical transformation without being consumed in the process. Catalysts may be in a gaseous, liquid, or solid state. In homogeneous catalysis, the catalyst is molecularly dispersed in the same phase (usually gaseous or liquid) as the reactants. In heterogeneous catalysis, the reactants and the catalyst are in different phases, separated by a phase boundary. The most commonly used heterogeneous catalysts are solids, and the reactants are in gaseous or liquid states. On the other hand, most of the processes using homogeneous catalysts occur in a liquid phase. The fact that the catalyst is in a distinct phase with respect to the reaction medium accounts for the major advantage of the heterogeneous catalysts over the homogeneous as it makes the separation of heterogeneous catalysts simple and cost-effective compared to the homogeneous catalysts [1].

Solid inorganic acids have been used for various chemical processes and catalytic systems because catalysis has played a major role in preventing pollution in our environment. Recently, a wide range of solid acids and their supported forms have been reported and extensively reviewed for various chemical processes [2, 3]. Owing to their possible utilization as alternatives to liquid inorganic acids in industry, solid acid catalysts have received much consideration [4–6]. They have the advantages of easy separation of the catalyst from the liquid reaction media, applicable recyclability, low corrosion, green chemical procedures, and improved product selectivity [7–9].

 SnO_2/SiO_2 nanocomposite has several advantages such as high thermal stability, high surface area, small in size, and non-toxic; therefore, it has been used as a catalyst in various types of reactions such as aminolysis of styrene oxide with aniline for the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone [10], hydroxylation of phenols [11], Baeyer–Villiger oxidations [12], Meerwein–Ponndorf–Verley reductions [13], sugar isomerization [14], epimerization [15], oxidative dehydrogenation of cyclohexane [16], and Cannizzaro-type reactions [17].

The non-aqueous synthesis of $\text{SnO}_2/\text{SiO}_2$ material is not well studied till date, and only a few reports are available for its synthesis. The first describes a procedure based on the reaction of TEOS with Tin (IV) acetate in anhydrous acetic acid [18]. Another report introduces a twin polymerization method for the production of $\text{SnO}_2/\text{SiO}_2$ [19]. The nanosized SnO_2 particles have been prepared by using different chemical methods such as precipitation and sol–gel [20, 21]. Tin oxide and tin oxide-supported metal oxide have been extensively used as solid acid or redox catalysts for the oxidative dehydrogenation of propane, CO oxidation, esterification reaction, reduction of NO/NO₂ to N₂, and hydrogenation reaction of nitrate [22–24]. Tin oxide has been more commonly used as a catalyst for the oxidation of organic compounds [25]. Multicomponent reactions (MCRs) have attracted considerable attention due to their ease of performance, high yield, and especially synthetic feasibility and efficiency [26–32]. MCRs include three or more starting materials reacting in a single flask to form a new product, where basically all the atoms contribute to the newly formed product. Due to the diverse biological activity of compounds in this class, there is great interest in their synthesis. There is a continuous widespread interest in the synthesis of pyrano-pyrimidinones because of the diverse biological properties associated with this system [33–46]. Compounds with such annulated uracils have antitumor, antihypertensive, antibacterial, and fungicidal activities, some of them exhibit antimalarial, antifungal, analgesics, and herbicidal properties [47–54].

Previous methods for the synthesis of 7-amino-2,4-dioxo-5-aryl-1,3,4,5-tetrahydro-2*H*-pyrano[2,3-*d*]pyrimidine-6-carbonitriles have been reported in which a twocomponent reaction between arylidene malononitrile with barbituric acid occurred under harsh thermal conditions [55]. Also, a microwave-assisted one-pot three-component cyclocondensation of barbituric acids, benzaldehyde derivatives, and alkyl nitrile in the absence or presence of triethylamine [56] has been reported. However, some of these methods are plagued by one or many drawbacks such as long reaction time, use of volatile solvents, low yields, and harsh reaction conditions [57]. Therefore, it is necessary to develop an improved route for the synthesis of pyranopyrimidinones under mild reaction conditions.

Academic as well as industrial chemists are constantly trying to find appropriate sustainable replacements for expensive, toxic, hazardous, and environmentally damaging catalysts. Thus, more convenient, high-yielding, and eco-friendly catalysts are always in demand. Hence, many efforts have been developed during the last decade for accomplishing MCR by using environmentally benign heterogeneous catalysts. Heterogeneous catalysts have high selectivity, which is very desirable in chemical synthesis, as it may offer several advantages such as avoidance of protection steps, minimization of side reactions, as well as step of the reaction [58–65].

In continuation of our studies for the synthesis of solid acids nanocomposite materials and nanomagnetic catalysts and our quest toward the development of a new heterogeneous catalytic system for the synthesis of bioactive heterocycles [66-73]. Here, we report a SnO₂/SiO₂ catalyzed synthesis of pyrano[2,3-*d*]pyrimidinone derivatives using multicomponent cyclocondensation of aldehydes, malononitrile, and barbituric acid in ethanol at room temperature (Scheme 1). The noticeable advantage of the present work is that the method is simple, fast, and environmentally benign, and the catalyst was recovered and reused several times for the preparation of pyrano-pyrimidinones.

Results and discussion

To optimize the reaction conditions, the reaction of benzaldehyde, malononitrile, and barbituric acid is considered as a model reaction to examine the effect of various solvents, such as acetone, toluene, acetonitrile, methanol, and ethanol with SnO_2/SiO_2 catalytic materials. Among all the solvent screened for the condensation, it was



Scheme 1 Synthesis of pyrano[2,3-d]pyrimidinone derivative

Table 1Effect of varioussolvents	Entry	Solvent	Time (min) ^a	Yield (%) ^b
	2a	Acetone	120	50
	2b	Methanol	75	85
	2c	Ethanol	60	94
	2d	Toluene	130	60
	2e	Acetonitrile	70	87

^aAll reactions were carried out using SnO₂/SiO₂ at room temperature ^bIsolated yields

Table 2Effect of variousamount of catalyst	Entry	Catalyst	Time (min)	Yield (%) ^a
	3a	-	200	_
	3b	SiO ₂	180	35
	3c	SnO_2	90	80
	3d	10 wt% SnO ₂ /SiO ₂	80	90
	3e	15 wt% SnO ₂ /SiO ₂	60	94
	3f	$20 \text{ wt\% } \text{SnO}_2\text{/SiO}_2$	70	92
	D .:	Demolitica Demoliticado	(1	1 1/1

Reaction conditions Benzaldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol), catalyst (0.1 g), and ethanol 15 mL

^aIsolated yields

observed that ethanol found to be an excellent medium and furnishing the product in excellent yield (Table 1).

After optimization of the solvent effect, we have also studied the optimization of the amount of catalyst. However, in the absence of the catalyst, the formation of the desired product was not observed, Table 2 (entry (3a)). Initially, pure SiO₂ was used as a catalyst for the model reaction, and the results obtained were very poor. After that, pure SnO₂ was also used for the reaction, and the results with respect to yields were good but the time required to complete the reaction was high. As we used 15 wt% SnO₂/SiO₂ catalysts, the time required for the completion of the reaction ultimately reduced with an increase in the yield of the product. Interestingly, it was observed that different wt% (10, 20) of SnO₂ support on SiO₂ furnishes the poor yields of the product, and longer reaction time is needed for the completion of the reaction. Hence, 15 wt% SnO₂/SiO₂ (0.1 g) was sufficient to carry out the reaction.

The model reaction was also carried out by non-conventional methods like ultrasonication and microwave irradiation. In ultrasonication, the time required for the completion of the reaction is 55 min with 85% yields. Similarly, the model reaction was also carried out by microwave irradiation, and the completion of the reaction takes place in 8 min affording 82% yields. So, from our experimental study, it was observed that the reaction condition 15 wt% SnO₂/SiO₂ in ethanol at room temperature is more favorable compared to ultrasonication and microwave irradiation. Table 3 shows the comparative study of different catalysts, the merit of the present work that SnO_2/SiO_2 nanocomposite catalyst consists of non-toxic, clean, green synthesis, and simple workup procedure, and the catalyst can be recovered easily.

To explore the scope and generality of the present method, a variety of different substituted aromatic aldehydes possessing electron-rich and electron-deficient groups as well as heterocyclic aldehydes gave good-to-excellent yields (90–95%) and the reaction was completed within 60–80 min in ethanol at room temperature (Table 4).

Then, we turned our attention toward the recovery and reusability of the catalyst (Fig. 1) as it is important from an industrial and economical point of view. The catalyst was separated, washed with *n*-hexane, and dried at 80 °C for 2 h before the next catalytic run. The reusability of the catalyst was investigated three times, and it was found to retain almost consistent activity (Table 4, entry **4a**).

To explain this mechanism, Knoevenagel condensation followed by cyclization leading to xanthene derivatives is accredited to the exclusive role of $\text{SnO}_2/\text{SiO}_2$ as a catalyst and is shown in Fig. 2. As $\text{SnO}_2/\text{SiO}_2$ is an acidic catalyst, initially benzaldehyde **1a** was partially bound with $\text{SnO}_2/\text{SiO}_2$ to activate carbonyl carbon followed by C=C bond formation with active methylene group of malononitrile **2** to form intermediate **I**. In the second step, the C–C bond formation of intermediates **I** with **3** to give the formation of intermediates **II**. In the next step, the intramolecular cyclization of intermediates II occurs to give intermediates III. In the last step, the protonation of the NH group to give the final product **4a** and the regeneration of the catalyst.

Experimental

All Chemicals were purchased either from Merck or Fluka and used without further purification. All products are known compounds and were characterized by comparing ¹H nuclear magnetic resonance (NMR) spectroscopic data and melting points with literature values. Uncorrected melting points of all compounds were measured in an open capillary in a paraffin bath. ¹H NMR spectra were recorded using a Bruker instrument (¹H at 400 MHz) in dimethyl sulfoxide (DMSO)-d6 solvent with tetramethylsilane (TMS) an internal standard. Thin-layer chromatography (TLC) was performed with silica gel 60 F254 plates with ultraviolet (UV) light for visualization. The morphology of the sample was characterized with CM-200 PHILIPS transmission electron microscopy (TEM) operated at 200 kV, resolution at 0.23 nm. FT-IR spectra were recorded on JASCO-FT-IR/4100, Japan, in KBr disc. The X-ray diffraction (XRD) patterns were recorded on Bruker 8D advance X-ray diffractometer using monochromator Cu-Ka radiation (40 kV and 30 mv) of wavelength = 1.5405 Å. Conventional scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) were obtained on JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA. Temperature-programmed desorption (NH₃-TPD) measurements were carried out on a Micrometrics Instrument corporation Chemisoft TPx V1.02 unit 1 (2750). The surface area of the samples was characterized by

Table 3 C	omparison of $\mathrm{SnO}_2/\mathrm{SiO}_2$ with other catalysts	or the synthesis of pyrano[2,3-d]pyrimidinone			
Entry	Catalysts and amount	Condition	Reaction time	Yields (%)	References
1	L-Proline (5 mol%)	Aqueous ethanol solvent and stirring rt	30–150 min	68-88	[74]
2	Ionic liquids (1.5 g)	Stirring at 90 °C	3–5 h	82–94	[75]
3	Nano SiO_2 (20 mol%)	Water solvent and thermal condition $(70 \circ C)$	19–30 min	89–94	[76]
4	DBA catalyst (20 mol%)	Aqueous ethanol solvent and stirring rt	53-110 min	83–94	[77]
5	$Zn[(L)proline]_2 (17 mol\%)$	Ethanol solvent and reflux	30 min-12 h	80–92	[78]
9	DAHP (10 mol%)	Aqueous ethanol solvent and stirring rt	2 h	06-02	[42]
7	$KAI(SO_4)_2$ ·12H ₂ O (alum 10% mol)	Water solvent stirring 80 °C	30–45 min	80–90	[80]
8	SBA-Pr-SO ₃ H, (0.02 g)	Solvent-free at 140 °C for oil batch	5-45 min	30–90	[81]
6	15 wt% SnO ₂ /SiO ₂	Ethanol solvent at stirring rt	50–80 min	91–95	Present work
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Entry	Aldehydes	Product	Time (min) ^a	Yield (%) ^a	M.P (°C)
4a	СНО		60	94 (93, 93, 92) ^b	207–209
4b	CHO		50	95	237–239
4c	CHO Br		55	95	229–231
4d	сно Сн ₃		70	91	225–227
4e	CHO F		65	91	226–228
4f			50	95	258–260
4g	CHO		80	92	212–214
4h	сно		60	90	240–242

 $\label{eq:table_table_table} \textbf{Table 4} \ 15 \ \text{wt\% SnO}_2/\text{SiO}_2 \ \text{catalyzed synthesis of pyrano-pyrimidinones reaction of benzaldehydes, malononitrile, and barbituric acid}$

 $Reaction\ conditions\ Benzaldehydes\ (1\ mmol),\ malononitrile\ (1\ mmol)\ barbituric\ acid\ (1\ mmol),\ catalyst\ (0.1\ g),\ and\ ethanol\ 15\ mL$

^aIsolated yields

^bYield after consecutive cycles



Fig. 1 The recyclability of SnO₂/SiO₂ in the synthesis of pyrano[2,3-d]pyrimidinone



Fig. 2 Plausible mechanism for the synthesis of pyrano[2,3-d]pyrimidinone

the BET analysis performing the adsorption of nitrogen at 77 K with Micrometrics ASAP 2010.

Preparation of pure Silica (SiO₂)

Silica samples were synthesized by using the sol-gel process. A quantity of (2.408 g) tetraethyl ortho-silicate (TEOS) was taken in an autoclave bottle to which 1% Cetyl trimethyl ammonium bromide (CTAB) in 20 mL ethanol was added dropwise with constant stirring. The reaction mixture was maintained at $pH \sim 10$ using aqueous ammonia. This mixture was then hydrothermally treated at 60 °C for 12 h

in an autoclavable bottle. After drying at 110 °C for 7 h in an oven, the obtained powder was pulverized using mortar and pestle and finally calcined at 400 °C for 2 h.

Preparation of SnO₂/SiO₂ catalyst

Series of SnO₂/SiO₂ nanocomposite catalytic materials were synthesized by using the sol–gel method. Generally, 15 wt% SnO₂/SiO₂ catalysts were synthesized by using (0.846 g) of Tin (IV) chloride dissolved in 20 mL double distilled water, and tetraethyl orthosilicate (TEOS) solution (2.408 g) was added dropwise in an autoclave bottle. The resulting mixture was stirred and 1% solution of cetyltrimethylammonium bromide (CTAB) in 20 mL ethanol was added dropwise with constant stirring. The reaction mixture was maintained at pH ~10 using aqueous ammonia. This mixture was then hydrothermally treated at 60 °C for 12 h in an autoclavable bottle. After drying at 110 °C for 7 h in an oven, the obtained powder was pulverized using mortar and pestle and finally calcined at 400 °C for 2 h. Similarly, 10 and 20 wt% SnO₂/SiO₂ catalysts were prepared in the same manner.

General procedure for the synthesis of pyrano-pyrimidinones 4(a-h)

A mixture of aldehydes (1 mmol, 0.106 g), malononitrile (1 mmol, 0.06 g) and barbituric acid (1 mmol, 0.128 g) catalytic amount of 15 wt% $\text{SnO}_2/\text{SiO}_2$ (0.1 g) in ethanol (15 mL) was stirred for the specified times mentioned in Table 4. The progress of the reaction was monitored by TLC (petroleum ether:ethyl acetate = 7:3 as eluent). After completion of the reaction, the reaction mixture was heated to solubilize the products. The catalyst is insoluble in ethanol; thus, the separation of the catalyst was easier by simple filtration. The filtrate was concentrated under reduced pressure, and the crude product obtained was recrystallized from ethanol to afford pure products **4(a-h)** (Scheme 1).

Spectroscopic data of representative compounds

7-Amino-2,3,4,5-tetrahydro-2,4-dioxo-5-phenyl-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile 4a ¹H NMR (400 MHz, DMSO-d₆): δ 4.44 (s, 1H), 5.81 (2H, br, s, NH₂), 6.91–8.28 (m, 5H), 10.38 (1H, br s, NH), 12.06 (1H, br s, NH). IR (KBr, cm⁻¹): 3203, 3174, 3076, 2202, 1710, 1630. ES-MS: *m*/*z* 283. 05 (M⁺).

7-Amino-5-(4-bromophenyl)-2,3,4,5-tetrahydro-2,4-dioxo-1H-pyrano[2,3-d]pyrimi*dine-6-carbonitrile* **4***c* ¹H NMR (400 MHz, DMSO-d₆): δ 4.42 (s, 1H), 5.69 (2H, br, s, NH₂), 6.88–820 (m, 4H), 11.05 (1H, br s, NH), 12.09 (1H, br s, NH) IR (KBr, cm⁻¹): 3207, 3153, 3091, 2195, 1693, 1678.

Catalyst characterizations

XRD analysis

Figure 3a–e shows the XRD patterns of synthesized materials. Figure 3a shows a broad peak at 22.27° corresponding to the amorphous nature of silica. Figure 3b for SnO₂ nanoparticles represents the XRD patterns for SnO₂ which show the presence of highly crystalline and sharp intense peaks, which are in good agreement with that obtained by JCPDS card no. 41-1445 [82] with lattice parameter a=4.743 Å and c=3.1859 Å. The crystal planes (110), (101), (211), (002), (310), and (301) were prominently seen in XRD indicating the polycrystalline nature of powder, suggesting the tetragonal lattice symmetry of these SnO₂ nanoparticles. No impurity phase was observed in all synthesized materials.

The same diffraction pattern was observed for all series of SnO₂/SiO₂ materials shown in Fig. 3c–e. It was found that as the loading of Sn in samples increases, a gradual increase exists in the peaks intensity (at $2\theta = 26.60^{\circ}$) for the plane (110) corresponding to the presence of SnO₂. Similarly, it was found that broad peaks at 22.71° in SnO₂/SiO₂ correspond to the presence of amorphous silica. From this, it is clearly seen that SnO₂ crystalline nanoparticles after depositing SiO₂ on its surface enhance porosity.

The average crystallite size (D) is determined from the XRD spectra using Scherrer's formula. The Scherrer equation [83–85] can be written as follows:



Fig. 3 (a–e) XRD patterns of (a) SiO₂, (b) SnO₂ and (c) 10 wt% SnO₂/SiO₂, (d) 15 wt% SnO₂/SiO₂, (e) 20 wt% SnO₂/SiO₂

$$\tau = K\lambda/(\beta \cos\theta)$$

where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; *K* is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM); θ is the Bragg angle (in degrees). Average crystallite size of the SnO₂ material was determined from the 110 plane at $2\theta = 26.6^{\circ}$ by using the Scherrer equation as shown in Table 5. It was seen that a pure sample of SnO₂ showed the crystallite size as 12.40 nm. As the loading of Sn increases, a gradual decrease in the crystallite size from 31.60 to 25.05 nm was observed for 10% and 15%, respectively. After that, for a 20% sample, small increase in the crystallite size 28.35 nm was observed.

TEM analysis

The morphological analysis of the synthesized material studied by TEM is depicted in Fig. 4a1–a4. The average particle size of all samples was investigated using the main linear intercept method by drawing random lines on the TEM photographs and counting the number of grain boundaries. Figure 4a1 shows that mesoporous silica having a particle size between 288 and 320 nm shows the presence of varying spherical shape which is a characteristic property of silica. Figure 4a2 shows the presence of flake-like SnO₂ nanoparticles with an average particle size of about 7–9 nm [86]. Figure 4a3 shows that the SnO₂ nanoparticles clearly deposited on spherical-shaped SiO₂ composite and therefore their particle size has ultimately reduced to about 25–30 nm. The particle size calculated from TEM was in close agreement with the particle size calculated from XRD and SEM. The typical SAED pattern for SnO₂ nanoparticle is depicted in Fig. 4a4 which indicates the presence of (110), (200), (211), and (310) planes, respectively, and predicts the tetragonal lattice symmetry of SnO₂ nanoparticles as evidenced from the XRD analysis.

SEM-EDS analysis

Figure 5b1–b3 shows the SEM analysis of synthesized materials. Figure 5b1 demonstrates that the surface morphological investigation of mesoporous silica shows good agglomeration of particles with a spherical shape, whereas Fig. 5b2 shows that

Table 5Average crystallite sizeof SnO_2 material determinedfrom the 110 plane by using theScherrer equation	Entry	Sample	Average crystallite size (nm)		
	1	SiO ₂	_		
	2	SnO_2	12.40		
	3	10% SnO ₂ /SiO ₂	31.60		
	4	15% SnO ₂ /SiO ₂	25.05		
	5	20% SnO ₂ /SiO ₂	28.35		



Fig. 4 a1-a4 TEM image of a1 SiO₂, a2 SnO₂, a3 15 wt% SnO₂/SiO₂, a4 diffraction patterns of SnO₂



Fig. 5 b1-b3 SEM image of b1 SiO₂, b2 SnO₂, b3 15 wt% SnO₂/SiO₂

 SnO_2 nanoparticles indicate a compact arrangement structure due to the uniform size which is responsible for importing irregular shapes [87]. The nanocomposite of 15 wt% SnO_2/SiO_2 (Fig. 5b3) shows the presence of some porosity which may be due to the insertion of SnO_2 particles on the surface of SiO_2 . This has helped in enhancing the catalytic activity of the material. The elemental analysis of 15 wt% SnO_2/SiO_2 (Fig. 6) shows the presence of constituent elements Sn, O, and Si confirmed on the basis of atom %, 3.65, 54.93, and 41.44, respectively. This indicates that the required stoichiometric ratio in the catalyst is maintained.



Fig. 6 EDS pattern of 15 wt% SnO_2/SiO_2

FT-IR analysis

Dry sample (10 mg) was ground with oven-dry KBr (200 mg), and the resulting homogeneous mixture (100 mg) was taken in the sample holder. The prepared sample was put in JASCO-FT-IR/4100, spectrometer and scanned between IR ranges 4000 and 400 cm⁻¹. Fig. 7a–e shows the FT-IR spectra of the prepared catalytic materials. Figure 7a shows the FT-IR spectrum of pure SnO₂ having an absorption band at 3205 cm⁻¹ which is due to the Sn–OH stretching vibration, and the band at 1634 cm⁻¹ is assigned for the Sn-OH bending vibration. Figure 7b shows that the FT-IR spectrum of pure SiO₂ gives infrared region at 3408 cm⁻¹ due to the Si–OH stretching vibration, 1620 cm⁻¹ due to the Si–OH bending mode, 1093 cm⁻¹ for Si–O stretching vibration, and 806 cm⁻¹ due to the Si–O–Si bending vibrational mode. The strong absorption band at 631 cm⁻¹ is due to the antisymmetric Sn–O–Sn vibrational mode of SnO₂. Similar results were reported in the literature by Deshpande et al. [88]. Similarly, Fig. 7c–e shows that the infrared bands at 3408, 1620, 1093, 806, and 631 cm⁻¹ are attributed to the SnO₂/SiO₂ framework.

TPD analysis

NH₃-TPD measurements were carried out by (i) pre-treating of samples from room temperature to 150 °C in Helium flow 25 cc/min for 1 h; (ii) adsorption of ammonia at room temperature; (iii) Desorption of adsorbed ammonia with a heating rate of 10 °C min⁻¹ starting from the adsorption temperature from 50 to 500 °C. The NH₃-TPD desorption was used to determine the acidic properties of solid catalysts. This provides information about the total concentration and strength of acidic sites (Bronsted and Lewis). From the TPD analysis, it was found that the ammonia desorbed in two different regions. In the first region, 0.06238 mmol/g of NH₃ desorbed at 259 °C to the presence of Lewis acidic sites, while in the second region 0.08625 mmol/g of NH₃ desorbed at 507.1 °C from Bronsted acidic sites. Hence,



Fig. 7 a-e FT-IR patterns of a SnO₂, b SiO₂, c 10 wt% SnO₂/SiO₂, d 15 wt% SnO₂/SiO₂, e 20 wt% SnO₂/SiO₂

the total strength of acidic sites present in 15 wt% SnO_2/SiO_2 was found to be 0.149 mmol/g (Fig. 8). It indicates that both Bronsted and Lewis acidic sites are present in SnO_2/SiO_2 composite materials.



Fig. 8 TPD profile of 15 wt% SnO₂/SiO₂



Fig. 9 BET surface area of 15 wt% SnO₂/SiO₂

Table 6 The acid strength and surface area

Entry	Catalyst	Total acidity (mmol/g)	Surface area (m ² /g)
1	15 wt% SnO ₂ /SiO ₂	0.149	331.5814

BET surface area

The N2-BET surface areas of 15 wt% SnO₂/SiO₂ material were characterized and shown in Fig. 9 and summarized in Table 6. The amount of N₂ gas adsorbed-desorbed at a given pressure allows to determine the surface area of the material. The isotherm for the prepared material indicates that a large volume was adsorbed on the surface of the material. The BET surface area observed is 331.5814 m²/g; similarly, Single Point Surface Area at P/Po 0.20128441 was found to be 327.5305 m²/g. It indicates that the material has a large surface area, and hence, this material shows a higher catalytic activity.

Similarly, BJH Adsorption Average Pore Diameter (4V/A): 22.1828 nm which indicates a large increase in pore size and surface area. The same result from XRD was observed, i.e., 25.05 nm. The pore volume is found to be $0.744036 \text{ cm}^3/\text{g}$, as shown in Fig. 10. It indicates that the formation of a porous surface, as well as the smaller pore volume of the material, may be due to the penetration of the silica into the pores of the SnO₂, which can be clearly seen in SEM and TEM images.

Reusability of catalyst

The catalyst was tested for its reusability with 15 wt% SnO_2/SiO_2 catalytic material. It was observed that there were no changes in its catalytic activity till the



Fig. 10 BJH adsorption average pore diameter of 15 wt% SnO₂/SiO₂

third cycle. It was clearly seen in the XRD of the material. There is a slight decrease in the crystalline nature of the catalyst, but all peaks are matched with the XRD of the fresh sample (Fig. 11).



Fig. 11 XRD pattern of reused 15 wt% SnO₂/SiO₂

Conclusion

In summary, an efficient catalytic system has been developed for the synthesis of pyrano[2,3-*d*]pyrimidinone derivatives from one-pot three component cyclocondensation of aromatic substituted benzaldehyde, malononitrile, and barbituric acid in ethanol at room temperature using 15 wt% $\text{SnO}_2/\text{SiO}_2$. The present method offers remarkable advantages such as non-toxic, non-corrosive, and inexpensive reaction conditions. Simple recovery and reusability of the catalyst make the reaction successful under environmental benign conditions.

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Compliance with ethical standards

Conflict of interest There are no conflict of interest to declare.

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