An Ultrasonic Accelerated Three-Component Condensation By KCC-1: A High Mechanical Stability Silica Nanospheres As A Good Catalyst For Ultrasonic Irradiation

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Research Article

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Abstract

Fibrous nano-silica sphere (KCC-1) has appeared as a good and efficient catalyst for ultrasonic irradiation conditions in chemical reactions. This catalyst has the unique properties such as a fibrous surface morphology, high surface area and high mechanical stability. The results indicated that the KCC-1 nanocatalyst could be used as high-performance catalysts under high temperature and pressure condition in organic reaction under ultrasonic irradiation. Morphology, structure, and composition of the fibrous nano-silica sphere were described by N2 adsorption–desorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FT-IR). In this work, we used KCC-1@NH$_2$ nanosilica as a basic catalyst for the preparation of chromenes under ultrasonic irradiation conditions for the first time. The recyclability, nontoxicity and high stability of the catalyst, combined with low reaction times and excellent yields, make the present protocol very useful for the synthesis of the title products under ultrasonic conditions. The produced products were confirmed via $^1$H NMR, $^{13}$C NMR, FT-IR analysis.

Introduction

In recent years, many studies have been concentrated on increasing the performance of organic catalytic synthesis because of their applicable importance. One of the progressive strategies which have recently attracted considerable attention is the usage of ultrasound conditions with heterogeneous catalysts. 2-Amino-4H-chromenes are an important class for further development in medicinal and organic synthesis studies due to their potency and a wide spectrum of biological activities including cancer therapy$^{1,2}$, antiviral$^{3,4}$, antitumor$^5$ and sex hormone$^6$. For example (Figure 1), pyranopyranone (1) as an ancestor for the blood anticoagulant warfarin,$^7$ (4H-chromen-4-yl)cyanoacetate (2) as inhibitor of Bcl-2 protein and apoptosis inducer$^8$ and benzopyran (3) has been known for anticancer therapeutic.$^9$ Also compounds 4 and 5 showed in Figure 1 the maximum inhibitory effect against the HT29 human colon cancer cells.$^{10}$ Chromenes have been used for the treatment of different diseases of connective tissues, diabetes, psoriasis, pernicious anemia, ulcerous colitis, and chronic hepatitis.$^{11}$ These derivatives are employed as a building block of many natural products$^{12,13}$, food additives, Pigments, Pesticides, cosmetic agents and potentially biodegradable agrochemicals$^{14}$.

The preparation of 2-Amino-4H-Chromenes has been reported using various conditions and catalysts such as piperidine$^{15,16}$, piperazine$^{17}$, triethyl amine$^{18}$, IL$^9$, MCM-41$^{20}$, K$_2$CO$_3$$^{21}$. Most of the reported methods need long reaction times, use of toxic solvents, low yields, non-reusable catalysts and stoichiometric reagents. In the present paper, we utilized acoustic cavitation. That is a physical phenomenon that helps chemical reactions under ultrasound irradiation. Ultrasound has been known as significant for green and remarkable synthetic methods.$^{22–24}$ The ultrasound approach reduces times, increases yields of products by creating the activation energy in micro surroundings.$^{25,26}$ This
phenomenon is generally contained the construction, growth, and transient implosive collapse of the gas and vapour filled microbubbles. The physical and chemical effects of cavitation are exciting for various applications.\(^ {27}\)

This method indicates bubble-sphere interaction on a microscale. The presence of suspended spherical particles near to substances of reactant could potentially have an important effect on bubble dynamics.\(^ {28,29}\) Precipitate implosion of these bubbles in the liquids creates localized hot spots with very short lifetimes. The hot spot has an equivalent temperature of 5000°C and pressure of about 2000 atmospheres can achieve upon the destruction of the bubble.\(^ {30}\) In this condition, the physical properties of the catalyst, including good thermal, hydrothermal, and high mechanical stabilities are very important.

Catalyst scientists and nanotechnology have helped a lot in this regard. Importantly, in our search of nanocatalysts, we used dendritic silica nanospheres (KCC-1) as the catalyst.\(^ {31-33}\) Fibrous nanosilica sphere (KCC-1) compared to MCM-41 and SBA-15-supported catalysts, shows excellent physical properties, including a high surface area, a fibrous surface morphology, good thermal/hydrothermal properties and high mechanical stability. The fibrous morphology observed in these nanospheres making it easily accessible. Dendritic silica nanospheres endure unaffected even after mechanical compression up to 216 MPa pressure whereas the conventional MCM-41 type of silica, which is endured at pressure 86 Mpa.\(^ {32}\)

In the synthesis of fibrous nanosilica (KCC-1), we can control particle size, fiber density, surface area and pore volume of KCC-1 and tune by changing various reaction parameters, such as the concentrations of urea, CTAB, 1-pentanol, reaction time, temperature, solvent ratio, and even outside stirring time.\(^ {34}\) KCC-1 can be used as catalyst support, sorbent or carrier. Due to the unique properties of silica is used in various organic reactions,\(^ {35-38}\) drug delivery systems and biomedical applications,\(^ {39}\) optoelectronic devices,\(^ {40}\) modern industries,\(^ {41-44}\) gas capture, solar energy harvesting\(^ {45,46}\) and many others. All in all, it is the fibrous morphology of KCC-1 that produces better accessibility of the active sites for enhanced catalytic activities and recovery efficiencies. As well as the mechanical and thermal stability of KCC-1 that provides the better heterogeneous catalyst for ultrasonic irradiation conditions. We chose, the ultrasonic route for the synthesis of 2-amino chromenes with modified dendritic silica nanosphere with amine groups present on the surface (KCC-1@NH\(_2\)) and distinct factors such as time of ultrasonic reaction and power of ultrasound utilized for optimizing the condition of reaction.

## Results And Discussion

### Structural analysis of the KCC-1@NH\(_2\) nanocatalyst

In this study, first fibrous nanosilica spheres was prepared with the methods was reported by Bayal and coworkers.\(^ {34}\) In the second stage, a NH\(_2\) shell using APTES (aminopropyltriethoxysilane) was coated on
the nanosilica core. The KCC-1@NH$_2$ nanocatalyst was as an efficient basic catalyst for the preparation of 2-Amino-4H-chromenes (scheme 1).

The IR patterns of different stages of nanosilica preparation are showed in Fig. 2. The characteristic peaks of the silica-based materials could be observed in the range of 1092 to 1150 cm$^{-1}$ representing the Si-O-Si asymmetric stretching while a Si-OH peak is observed at 812 cm$^{-1}$, which represents the stretching vibration and symmetric bending (Fig. 2b). In addition, the peaks at around 2930 cm$^{-1}$ can be assigned to the -CH stretching frequency derived from the CH$_2$ groups of the alkyl chains (Fig. 2c). These FT-IR spectral features indicated the successful functionalization of APTES over KCC-1.

The XRD pattern of nanosilica spheres (KCC-1@NH$_2$) is depicted in Fig. 3. This figure reveals high phase purity of the nanocatalyst and has a perfect agreement with the reported XRD pattern for nanosilica spheres (KCC-1@NH$_2$) (JCPDS No. 71-1232). The XRD pattern of KCC-1@NH$_2$ includes peaks from SiO$_2$ and Organic layer on this catalyst. The average crystalline size of the nanocatalyst was calculated to be 8 nm that was obtained from FWHM Scherrer's formula.

The elemental compositions of the brous nanosilica spheres (KCC-1@NH$_2$) were demonstrated by EDX. Energy Dispersive Spectroscopy (Fig. 4) confirmed the presence of Si, O, C and N in the nanocatalyst. By the scanning electron microscopy (SEM) image, morphology, and particle size of brous nanosilica spheres (KCC-1@NH$_2$) is confirmed (Fig. 5). Figure 5a indicates a FE SEM image of nanosphere KCC-1@NH$_2$ samples, where the samples have spheres of uniform size with average diameters of 95 nm and the nanoparticles show good dispersity with spherical morphology. The SEM image of the reused catalyst for six runs is shown in figure 5b. This image is confirmed the high stability of the reused nanocatalyst after five runs.

The TEM image of the KCC-1@NH$_2$ nanocatalyst (Figure 5d) demonstrates that wrinkled fibers grow out from the center of the spheres and are arranged radially in three dimensions. The TEM image provides more exact information about the particle size and morphology of the nanomaterial. The TEM image tells the spherical shape of the nanosilica, with an average size of 97 nm, which shows near agreement with the value determined via SEM. The FE SEM and TEM image indicates that the entire sphere is solid and composed of spherical.

Nitrogen adsorption-desorption isotherms analysis and BJH pore size distributions are done to evaluate the surface and structure properties of KCC-1@NH$_2$ (Figure 6). According to the International Union of Pure and Applied Chemistry (IUPAC) classification, this catalyst indicated characteristic type IV curve, which is consistent with literature reports on standard fibrous silica spheres. H2 type hysteresis loop in the relative pressure ranges from 0.4 to 1.00, is attributed to mesopore materials. For KCC-1@NH$_2$, the BET surface areas were 297 m$^2$ g$^{-1}$; pore diameters were 8.32 nm; and pore volumes 0.62 cm$^3$ g$^{-1}$, respectively.
The thermal behavior of nanosilica spheres (KCC-1@NH₂) is shown in Figure 7. The TG profile exhibits two steps of weight loss. The initial mass loss of 5% accrued with an endothermic peak in DTA curve is revealed in the temperature range of 80–144°C. It can be related to the release of physically absorbed water or solvent on the surface of the KCC-1@NH₂ and other raw materials. The second mass loss of 20% in a wide temperature range of 440–640°C was overlapping a broad endothermic DTA peak. It corresponds mainly to the thermal decomposition of the organic group. The results of the thermal analysis expressed that the thermal decomposition of organic moiety completed at a temperature of 823°C.

**Synthesis of 2-amino-4H-chromenes catalyzed by nanosilica KCC-1@NH₂**

Chromenes derivatives have been prepared from the Knoevenagel condensation of 1,5-naphtalenediol, malononitrile and aromatic aldehydes compounds catalyzed by nanosilica at 20 kHz frequency and 80 W power for an appropriate time under ultrasound irradiation as drawn in Scheme 2.

The effect of experimental factors comprising type and amount of catalyst, different powers of ultrasound irradiation, different solvents and effects of different donor or withdrawing substitutions of aldehydes were investigated to find the best condition for this reaction and the results are listed in Tables. For this purpose, the reaction between 4-chlorobenzaldehyde (1.0 mmol), malononitriles (1.0 mmol), and 1,5-dinaphtol (0.5 mmol) as substrates by prepared nanosphere as a catalyst under ultrasonic conditions was selected as the model reaction. At first, the optimum amount of catalyst was investigated in ethanol solvent (Table 1).

With reference to the results shown in Table 1, the optimized quantity of nanocatalyst for this synthesis is 0.05g (Table 1, entry 5). In an effort to obtain better yields and the most effective solvent, various solvents were used for the synthesis of chromenes. The examination of solvent was demonstrated that ethanol as protic solvent is the best condition for the Knoevenagel condensation of benzaldehydes and malononitrile compounds (Table 1, entry 5). Comparison of this entry with entries 8-9 of Table 1 (various catalysts containing piperidine and NEt₃) reveals that the nanocatalyst is the most efficient catalyst for the sonochemical synthesis of 2-amino chromenes.

Evaluation of thermal and ultrasound conditions shows that the ultrasonic approach is very effective for this synthesis is presented in Table 1. When the 2-Aminochromenes derivatives were synthesized under the heating method (entry 10, Table 1), they were produced in lower yields at higher reaction times, but performing these reactions under sonication conditions created excellent yields of 2-Aminochromenes at short times. Therefore, because of its basic green chemistry conception, the shock wave and microjet generated by the cavitation, this method is more environmentally benign. During the ultrasonic irradiation, KCC-1@NH₂ nanocatalyst like a wall for the transmission of the bubble, is dispersed in the reaction and...
affords more sites for the generation of the number of micro-bubbles. Increasing of micro-cavities may advance the helpfulness of the ultrasound approach to the formation of 2-Aminochromenes.\textsuperscript{35–38}

In continues, to detect the suitable power of ultrasonic irradiation for this reaction, it was tested under different powers of ultrasound irradiation as shown in Table 2. In the end, this reaction is effectively proceeded by 0.05g of KCC-1@NH\textsubscript{2} nanocatalyst with the power of 80 W of ultrasonic irradiation. Really in ultrasound irradiation the number of active cavitation bubbles and size of the individual bubbles is to increase. As a result, collapse temperature was increased and accelerated the synthesis of 2-aminochromenes derivatives reaction. Various substituted 2-Aminochromenes were prepared by nanocatalyst using the obtained optimized condition (Table 3). The results were indicated that aromatic aldehydes with electron-withdrawing groups reacted much more faster compared to those with electro-donating groups.

A rational mechanism for the preparation of 2-Aminochromens under ultrasonic irradiation by the KCC-1@NH\textsubscript{2} nanocatalyst is illustrated in Scheme 3. At first, a complex was formed between the carbonyl group of aldehyde and the NH\textsubscript{2} group of nanocatalysts. Also, acidic hydrogen of malononitrile was removed. Afterward, by a Knoevenagel condensation, active methylene of malononitrile attacked to aldehyde and affords to intermediate I after removing one molecule of H\textsubscript{2}O. Then, 1,5-dinaphthol from β-position attacks to the cyanoolefin compound (I) to give II. Finally, further aromatization and intramolecular cyclization of II gives III which is converted to the corresponded product. These steps are efficiently offered on the cavitation effect of ultrasound irradiation and also by the high nanosphere surface. Based on this mechanism, it is highly probable that the carbonyl groups of aldehydes and malononitrile compounds have been activated, by the coordination of carbonyl oxygen and KCC-1@NH\textsubscript{2} nanospheres. Thus KCC-1@NH\textsubscript{2} nanospheres activated of methylene of malononitrile and carbonyl groups. Due to its high surface area increase the rate and yield of the reaction. In addition, the catalyst used is easily filtrated and reused without any noticeable loss of activity after at least five times (Scheme 3).

**Reusability of KCC-1@NH\textsubscript{2} nanocatalyst**

Reusability and recoverability of Nanosilica spheres (KCC-1@NH\textsubscript{2}) are known as one of the most important properties of the catalyst under ultrasonic conditions. After the completion of reaction, 5 mL of acetone was added to the reaction mixture. The product solved in acetone and nanosilica was recycled via filtration. The reusability of our catalyst was tested for the model reaction, and it was found that product yields lessened only Nanosilica spheres (KCC-1@NH\textsubscript{2}) are recoverable without a considerable loss of catalytic activity (Fig. 8). It was very important to us that the catalyst was stable in ultrasonic irradiation conditions. Accordingly, we investigated the morphology and particle size of the nanocatalyst before use and after reuse six times in reaction by SEM image as presented in Figures 5b and 5c. According to the figures, the morphology of the nanoparticles stayed unchanged. We believe this is also
the possible reason for the extreme stability of the fibrous nanosilica spheres for ultrasonic irradiation conditions.

In Table 4 was showed different reports in the literature for the synthesis of 2-amino chromenes. Table 4 represents the differences between their results (entries 1-4) and the results of the present research (entry 5). As can be seen the proposed method in this work is the best condition for the synthesis of 2-amino chromenes derivatives. The properties such as mild reaction condition, high yields of 2-amino chromenes, easy recovery of the nanosilica by filtration, reusability of the catalyst for 6 times without significant loss of catalytic performance, short reaction times and environmentally benign of this method makes better than other previous methods. The main drawback of other procedures is a non-reusable catalyst, long reaction time, difficulty in separation of catalyst from the reaction mixture and low efficiency.

**Experimental Section**

**Substances and method**

Cetyltrimethylammonium bromide (CTAB) \(\{(\text{C}_{16}\text{H}_{33})\text{N(CH}_{3}\text{)}_{3}\}\text{Br}\), Urea, Tetraethyl orthosilicate \((\text{Si(OC}_{2}\text{H}_{5})_{4}\), Merck, >98\%), Cyclohexane, hexanol, (3-Aminopropyl) triethoxysilane (APTES), dried Toluene \((\text{C}_{7}\text{H}_{8}\), Merck, >99.8\%), absolute Ethanol \((\text{C}_{2}\text{H}_{5}\text{OH}\), Merck, >99.9\%), Malononitril, 1,5-dihydroxynaphthalene, derivatives Aldehyde were acquired from Merck and Sigma-Aldrich Company. They were used immediately without further filtration and distilled water was used throughout the test.

In this reaction, we were applied the ultrasonic irradiation using a multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), armed by a converter/transducer and titanium oscillator (horn), 12.5mm diameter, operating at 20 kHz with a maximum power output of 200 W. The ultrasonic generator automatically harmonized the power level. Melting points of synthesized products were determined by Electrothermal 9200. IR spectra of synthesized products and different stages of catalyst fabrication were noted by means of FT-IR Magna spectrometer 550 Nicolet using KBr plates. \(^{13}\text{C}\) NMR and \(^1\text{H}\) NMR spectra were reached in DMSO-\(d_6\) as a solvent on Bruker Avance-400 MHz spectrometers in TMS as an internal standard. The microscopic morphology of the nanoparticles was visualized by the morphological features of the sample were investigated with a Zeiss (EM10C -Germany) transmission electron microscope (TEM) operating at 100 kV and field emission scanning electron microscopy (FE SEM) (MIRA 3 TESCAN). Energy-dispersive X-ray spectroscopy (EDX) of the nanoparticles was imagined by a Sigma ZEISSL, Oxford Instruments Field Emission. For surface area measurement was used of Brunauer Emmett Teller (BET) method. It was determined by nitrogen adsorption amount using a mechanized gas adsorption analyzer (Tristar 3000, Micromeritics). Powder XRD of KCC nanoparticles was achieved by a Philips diffractometer of X’pert Company. Thermogravimetric and differential thermal analysis (TGA-DTA) were obtained from a Bahr STA-503 instrument in the air at a heating rate of 10°C min\(^{-1}\). The purity determination of the substrates and reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates (from Merck Company).
Preparation of Fibrous Nanosilica Spheres (KCC-1)

Bayal and coworkers reported the methods of synthesizing of KCC-1\textsuperscript{34}. Briefly, 1 g CTAB was added to 10 mL deionized water and after 0.6 g urea was added to the flask, the mixture was stirred for about 3 h at room temperature. Then, the mixture of 2 g TEOS, 1.5 mL hexanol and 30 mL cyclohexane was added to the flask and sonicated for 30 min. Later, the mixture was refluxed at 120 °C for 4 h and afterward refluxed at 80 °C for 24 h. Then, the mixture was cooled to room temperature and centrifuged to collect the KCC-1 as white sediment. The collected KCC-1 was washed several times with water and ethanol and dried at 60 °C for 24 h. Finally, KCC-1 was calcinated at 550 °C for 6 h to remove the CTAB as a templating agent. For this mechanism, urea was added to hydrolyze the TEOS to produce negatively charged \((\text{SiO}_4)_{4}^-\) silicate. Using of CTAB persuades the silicate molecules to form self-assembled linear structures where the CTAB helps to the aggregating of the silicates\textsuperscript{32,47}

Preparation of KCC-1@NH\textsubscript{2}

To functionalize the KCC-1 surface with NH\textsubscript{2} moieties, 0.02 g of KCC-1 was dispersed on 1.2 mL dried toluene and sonicated for 30 min. Then 50 µL 3-aminopropyltriethoxysilane (APTES) was added to the mixture and refluxed for 20 h at 80 °C. Then the mixture was separated and washed with toluene several times and dried at 80 °C for at least 24 h\textsuperscript{48}.

General procedure for the preparation of 2-Amino-4H-chromenes using functionalized Fibrous Nanosilica Sphere (KCC-1@NH\textsubscript{2}) under ultrasonic irradiation

A mixture of 1,5-naphtalenediol (1 mmol), malononitrile (2 mmol) and aromatic aldehydes (2 mmol) and Fibrous Nanosilica Sphere(KCC-1@NH\textsubscript{2}) (0.05 g) as a catalyst in ethanol (5 mL) was sonicated at 20 KHz frequency and 80 W power for required times. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture dissolved with acetone. Then, nanocatalyst was filtered and washed with toluene, dried and re-used for a successive run under the same reaction conditions. Evaporation of the solvent of the residual solution under reduced pressure gave a crude product. The solid product was recrystallized with EtOH to get pure product. The products were characterized based on \(^1H\)-NMR, FT-IR, and melting point analysis, and the spectral data of the synthesized compounds were compared with authentic samples. The Spectra data of new compounds are presented:

Spectral data.

3,9-diamino-1,7-bis(3-chlorophenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4d): 92%, Yellow solid, m.p = 310-315°C (decomp.), IR (KBr) ν (cm\textsuperscript{-1}): 3439 (NH\textsubscript{2}), 3327 (NH\textsubscript{2}), 3198, 2195(CN), 1649 (NH\textsubscript{2} bending), 1595, 1474, 1385, 1280, 1187, 1080 (C-O), 893, 753; \(^1\text{H}\) NMR (DMSO-d6, 400 MHz) δ
(ppm): 4.97 (s, 2H, CH\textsubscript{benzyl}), 7.17-7.35 (m, 10H, H\textsubscript{aromatic}), 7.24 (br.s, 4H, NH\textsubscript{2}), 7.88-7.90 (dd, J = 8.4 Hz, 2H, H\textsubscript{aromatic}).

3,9-diamino-1,7-bis(3-hydroxyphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4f): 90%, Yellow solid, m.p. >300°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3444 (NH\textsubscript{2}), 3301 (NH\textsubscript{2},OH), 2192 (CN), 1652 (NH\textsubscript{2} bending), 1596, 1455, 1386, 1280, 1246, 1187, 1081 (C-O), 886, 761; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta (ppm): 4.78 (s, 2H, CH\textsubscript{benzyl}), 6.67-6.69 (m, 4H, H\textsubscript{aromatic}), 7.07-7.10 (m, 4H, H\textsubscript{aromatic}), 7.13 (br.s, 4H, NH\textsubscript{2}), 7.22-7.24 (m, 2H, H\textsubscript{aromatic}), 7.86-7.88 (dd, J=8.4 Hz, 2H, H\textsubscript{aromatic}), 9.35 (s, 2H, OH).

3,9-diamino-1,7-bis(4-hydroxyphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4g): 87%, Yellow solid, m.p. >300°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3422 (NH\textsubscript{2}), 3323 (NH\textsubscript{2},OH), 2923, 2180 (CN), 1655 (NH\textsubscript{2} bending), 1595, 1511, 1389, 1255, 1184, 1085 (C-O), 759; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta (ppm): 4.75 (s, 2H, CH\textsubscript{benzyl}), 6.67-6.69 (d, J = 8 Hz, 4H, H\textsubscript{aromatic}), 7.00-7.02 (d, J = 8 Hz, 4H, H\textsubscript{aromatic}), 7.06 (br.s, 4H, NH\textsubscript{2}), 7.17-7.20 (d, J = 8.8 Hz, 2H, H\textsubscript{aromatic}), 7.83-7.85 (d, J =8.4 Hz, 2H, H\textsubscript{aromatic}), 9.34 (s, 2H, OH).

3,9-diamino-1,7-bis(2-hydroxyphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4h): 85%, Yellow solid, m.p. >300°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3467 (NH\textsubscript{2}), 3332 (NH\textsubscript{2},OH), 3196, 2192 (CN), 1650 (NH\textsubscript{2} bending), 1596, 1461, 1383, 1280, 1187, 1080 (C-O), 889, 799; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta (ppm): 5.11 (s, 2H, CH\textsubscript{benzyl}), 6.91-6.93 (d, J=7.2 Hz, 2H, H\textsubscript{aromatic}), 6.98-7.01 (d, J=8.8 Hz, 2H, H\textsubscript{aromatic}), 7.27 (s, 4H, NH\textsubscript{2}), 7.39-7.43 (dd, J=8 Hz, 2H, H\textsubscript{aromatic}), 7.66-7.68 (d, J=8.4 Hz, 2H, H\textsubscript{aromatic}), 7.77-7.80 (d, J=8.8 Hz, 2H, H\textsubscript{aromatic}), 10.30 (s, 2H, OH).

3,9-diamino-1,7-bis(4-isopropylphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4i): 82%, Yellow solid, m.p = 315-320°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3492 (NH\textsubscript{2}), 3379 (NH\textsubscript{2}), 2198 (CN), 1651 (NH\textsubscript{2} bending), 1596, 1455, 1386, 1272, 1232, 1187, 1086 (C-O), 854, 763; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta (ppm): 1.14 (s, 6H, CH\textsubscript{3}), 1.16 (s, 6H, CH\textsubscript{3}), 2.80-2.83 (m, 2H, CH), 4.84 (s, 2H, CH\textsubscript{benzyl}), 7.12 (br.s, 4H, NH\textsubscript{2}), 7.13-7.27 (m, 10H, H\textsubscript{aromatic}), 7.85-7.88 (dd, J = 8.4 Hz, 2H, H\textsubscript{aromatic}).

3,9-diamino-1,7-bis(4-methylphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4j): 85%, Yellow solid, m.p =310-320°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3454 (NH\textsubscript{2}), 3325 (NH\textsubscript{2},OH), 3202, 2922, 2196(CN), 1659 (NH\textsubscript{2} bending), 1596, 1500, 1388, 1282, 1238, 1187, 1084 (C-O), 854, 763; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta (ppm): 2.07 (s, 6H, CH\textsubscript{3}), 5.40 (s, 2H, CH\textsubscript{benzyl}), 7.09-7.13 (m, 2H, H\textsubscript{aromatic}), 7.22-7.29 (m, 8H, H\textsubscript{aromatic and NH\textsubscript{2}}), 7.37-7.40 (m, 2H, H\textsubscript{aromatic}), 7.61-7.63 (dd, J=8 Hz, 2H, H\textsubscript{aromatic}), 7.86-7.88 (dd, J = 8.8 Hz, 2H, H\textsubscript{aromatic}).

3,9-diamino-1,7-bis(4-nitrophenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8 dicarbonitrile (4l): 94%, Yellow solid, m.p. >300°C (decomp.), IR (KBr) \nu (cm\textsuperscript{-1}): 3441 (NH\textsubscript{2}), 3336 (NH\textsubscript{2}), 3196, 2190(CN), 1655 (NH\textsubscript{2} bending), 1597, 1527, 1387, 1350, 1281, 1187, 1082 (C-O), 800, 728; \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz) \delta
(ppm): 5.21 (s, 2H, CH\textsubscript{benzyl}), 7.28-7.30 (m, 4H, H\textsubscript{aromatic}), 7.34 (br.s, 4H, NH\textsubscript{2}), 7.60-7.73 (m, 6H, H\textsubscript{aromatic}), 7.90-7.92 (d, J = 8 Hz, 2H, H\textsubscript{aromatic}), 8.12 (br.s, 2H, H\textsubscript{aromatic}).

3,9-diamino-1,7-bis(2,3-dimethoxyphenyl)-1,7-dihydrochromeno[8,7-h]chromene-2,8-dicarbonitrile (4n):
83%, Yellow solid, m.p > 300°C (decomp.), IR (KBr) ν (cm\textsuperscript{-1}): 3430 (NH\textsubscript{2}), 3315 (NH\textsubscript{2}), 2195 (CN), 1654 (NH\textsubscript{2} bending), 1599, 1477, 1386, 1284, 1077 (C-O), 766; \textsuperscript{1}H NMR (DMSO-d6, 400 MHz) δ (ppm): 3.55 (s, 6H, CH\textsubscript{3}O), 3.73 (s, 6H, CH\textsubscript{3}O), 5.06 (s, 2H, CH\textsubscript{benzyl}), 6.62-6.64 (d, J = 8 Hz, 2H, H\textsubscript{aromatic}), 6.87-6.89 (dd, J = 8 Hz, 2H, H\textsubscript{aromatic}), 6.94-6.98 (dd, J = 8 Hz, 2H, H\textsubscript{aromatic}), 7.07 (br.s, 4H, NH\textsubscript{2}), 7.11-7.13 (d, J = 8.4 Hz, 2H, H\textsubscript{aromatic}), 7.81-7.83 (d, J = 8.4 Hz, 2H, H\textsubscript{aromatic}).

**Conclusion**

In the current study, we introduced dendritic silica nanomaterials (KCC-1) with fibrous pore structure possess as a mild, efficient, high activity and stability catalyst for the one-pot synthesis of 2-Amino chromenes by multicomponent reactions under ultrasonic irradiation. This enhancement in activity was explained on the basis of the excellent accessibility of the active sites due to the open and flexible fibrous structure of KCC-1, as well as the different amine groups present on the surface. The novel fibrous nanosilica spheres (KCC-1) nanocatalyst was characterized using FT-IR, SEM, TEM, EDX, XRD, TGA and BET techniques. The catalyst showed excellent efficiency and could convert >92% of the substrates to the target molecules. We believe, our procedure will find important applications in the synthesis of 2-Amino chromens, which represents a major advantage for reactions from the stability of this catalyst and short reaction time for synthesis of heterocyclic compounds using ultrasonic irradiation. This method offers several advantages including heterogeneous, easy separation, thermal stability, high surface area and resistance of the catalyst under ultrasonic irradiation, short reaction time, simple experimental workup procedure, lower loading of the catalyst compared with the other methods, easy product separation, and purification, which makes it a suitable process for the synthesis of 2-amino chromens.

**Declarations**

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Tables
Table 1
Optimization of reaction condition for the formation of 2-amino-4H-chromenes \(^{a,c}\)

| Entry | solvent | Catalyst (g)                  | Time (min) | Yield\(^{b}\)% |
|-------|---------|-------------------------------|------------|-----------------|
| 1     | DMF     | Nano KCC-1@NH\(_2\) (0.05)   | 20         | 80              |
| 2     | CH\(_3\)CN | Nano KCC-1@NH\(_2\) (0.05)   | 20         | 80              |
| 3     | H\(_2\)O | Nano KCC-1@NH\(_2\) (0.05)   | 20         | 90              |
| 4     | THF     | Nano KCC-1@NH\(_2\) (0.05)   | 20         | 60              |
| 5     | EtOH    | Nano KCC-1@NH\(_2\) (0.05)   | 20         | 96              |
| 6     | EtOH    | Nano KCC-1@NH\(_2\) (0.08)   | 20         | 96              |
| 7     | EtOH    | Nano KCC-1@NH\(_2\) (0.03)   | 20         | 90              |
| 8     | EtOH    | TEA                           | 20         | 85              |
| 9     | EtOH    | piperidine                    | 20         | 85              |
| 10    | EtOH    | Nano KCC-1@NH\(_2\) (0.05)   | 180        | 70              |

\(^a\)Reactions conditions: p-chloro benzaldehyde (1 mmol), 1,5- naphtalendiol (0.05 mmol), malononitrile (1 mmol)

\(^b\)Isolated yield

\(^c\)Ultrasonic irradiation (80 W)
Table 2
Optimization of reaction condition for the formation of 2-amino-4H-chromenes $^{a,c}$

| Entry | Power (W) | Time (min) | Yield (%)$^b$ |
|-------|-----------|------------|---------------|
| 1     | 50        | 20         | 45            |
| 2     | 60        | 20         | 65            |
| 3     | 70        | 20         | 82            |
| 4     | 80        | 20         | 96            |
| 5     | 90        | 20         | 96            |

$^a$Reactions conditions: p-chloro benzaldehyde (1 mmol), malononitrile (1 mmol), 1,5- dinaphtol compound (0.5 mmol), nano KCC-1@NH$_2$ (5 %)

$^b$Isolated yields

Due to technical limitations, table 3 is only available as a download in the Supplemental Files section.

Table 4. Comparison the results of synthesis of 2-Amino-chromens through the knoevenagel condensation in this research and various reports in the literature

| Entry | Catalyst$^a$ | Solvent | Reaction condition | Time (min) | Yield (%)$^b$ |
|-------|--------------|---------|--------------------|------------|---------------|
| 1     | Nano ZnO (0.5 mmol)$^{50}$ | H$_2$O | Thermal / 80$^\circ$C | 180 | 70            |
| 2     | KF/Al$_2$O$_3$ (0.5 g)$^{51}$ | EtOH | Thermal / 80$^\circ$C | 300 – 360 | 93            |
| 3     | TEA (2-3 drops)$^{18}$ | - | Microwave / 300 W | 5-6 | 82            |
| 4     | TEA (0.5 mL)$^{18}$ | EtOH | Thermal / 80$^\circ$C | 10 | 82            |
| 5     | Nano KCC-1@NH$_2$ (0.05 g) | EtOH | US / 80 W | 20 | 96            |

$^a$Literature references

$^b$Isolated yield

Schemes
Schemes 1-3 are available in the Supplementary Files section.

Figures

Figure 1

Structures of some 2-amino-4H-chromenes with diverse biological
Figure 2

The FT-IR spectra of (a) KCC-1 before calcination, (b) KCC-1 after calcination and (c) KCC-1@NH2
Figure 3

The XRD pattern of nanosphere KCC-1@NH2
Figure 4

The EDX spectrum of nanosphere KCC-1@NH2
Figure 5

The SEM image of nanosphere KCC-1@NH2 (a) KCC-1 (b) KCC-1@NH2 before use (c) after reuse of six times, and (d,e) TEM images of KCC-1@NH2.
Figure 6

The BET and BJH images of KCC-1@NH2

Figure 7
The TGA and DTA curves of KCC-1@NH2.

Figure 8

Recovery of nanosphere KCC-1@NH2

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.png
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- Graphicalabstract.jpg
- Scheme3.png
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