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ARTICLE TYPE

Synthesis and characterization of two novel biological-based nano organo solid acids with urea moiety and their catalytic applications in the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions

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2-Carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as novel, mild and biological-based nano organocatalysts with urea moiety were designed, synthesized and fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, elemental analysis, thermal gravimetric (TG), derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX), atomic force microscopy (AFM) and UV/Vis analysis. The catalytic applications of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid were studied in the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives *via* the condensation reaction of between several aromatic aldehydes and 1-phenyl-3-methylpyrazol-5-one (synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols)), the Knoevenagel condensation of Meldrum's acid with salicylaldehyde derivatives (synthesis of coumarin-3-carboxylic acids) and the condensation of Meldrum's acid with aromatic aldehydes (synthesis of cinnamic acids) under mild and solvent-free conditions. In the offered studies, some products were formed and reported for the first time. The described nano organo solid acids have potential for industrial production.

Introduction

It is broadly qualified that there is a growing significance for more ecologically sustainable approaches in the fine chemical processes, pharmaceutical industries, design, synthesis and applications of catalysts because catalysis has played a major role in the pollution prevention in our environment. This advanced extension well-known as 'green Chemistry' or 'sustainable development' requires a model shift from common contents of method efficacy, that attention mainly on yield of product, to one that gives economic value, removing waste and avoiding the usage of toxic or dangerous materials.[1-3] Furthermore the significant properties seen in water as an effect of its chemical and physical properties are very beneficial for selectivity and reactivity that cannot be achieved in other organic solvents and make it an efficient solvent for many organic reactions, not just for biochemical procedures.[4, 5] In the field of organic chemistry for example nucleoside, peptide or combinatorial synthesis, simply available amine protecting groups are frequently needed, which are stable under a wide range of reaction conditions and are simply and selectively cleavable.[6]

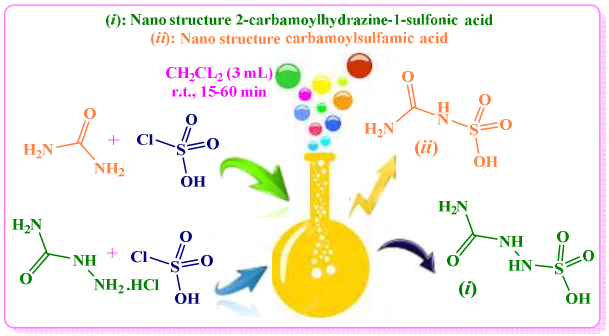
The design, synthesis and use of high efficiency catalysts in synthetic organic procedures counting metal-free organic molecules (organocatalysts) have possessed an important amount of affection from the scientific association so as to improve gradually noteworthy approaches for the synthesis of more complex molecules.[7] Organocatalysts have an important influence and straight advantage in the creation of pharmacological intermediates when compared with transition metal catalysts. Another advantage of organocatalysts relates to their favorable surface to volume ratio which enhances the contact between reactants and catalyst support and in turn increases the catalytic activity.[8-10]

On the other hand, heterocycles exhibit the chief of the typical sections in organic and bioorganic chemistry both industrially and biologically. Among of them, pyrazoles are a significant type of bio-active drug aims in the pharmaceutical industry, as they are the main structure moiety of various biologically active compounds.[11] For instance, they represent analgesic, antipyretic, anti-anxiety and anti-inflammatory properties. 2,4-dihydro-3*H*-pyrazol-3-one derivatives counting 4,4'-(arylm-ethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ols) have a wide spectrum of agreed biological activity, being applied as antidepressant,[12] gastric secretion stimulatory,[13] antipyretic,[14] antibacterial[15] anti-inflammatory[16] and antifilarial agents.[17] Furthermore, the analogous 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols) are used as secticides,[18] pesticides,[19] fungicides[20] and dyestuffs[21] and as the chelating and extracting reagents for numerous metal ions.[21]

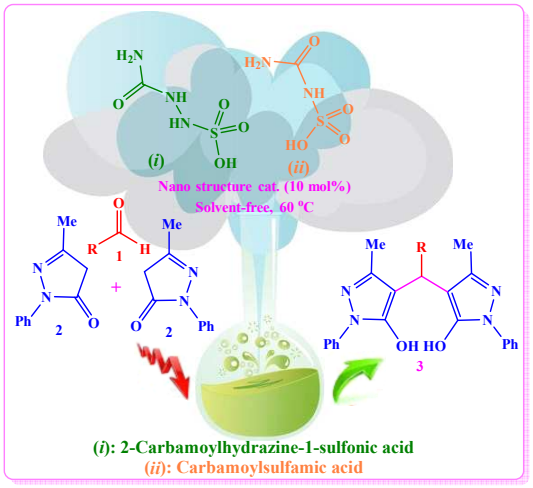
Coumarin derivatives have a wide range of uses in the perfume, pharmaceutical, and cosmetic industries.[22] Various carboxycoumarins have been applied as triplet sensitizers[23, 24] and fluorescent probes.[25, 26] Coumarin-3-carboxylic acid derivatives are significant original compounds for the synthesis of coumarins, which are identified natural products for their various biological activities.[27] Coumarin-3-carboxylic acids are usually synthesized *via* Knoevenagel condensation[28] of ortho-hydroxyaryl aldehydes with malonic acid,[28, 29] cyanoacetic ester[30] and malonic ester.[29, 31]

In biological chemistry, cinnamic acid is a main intermediate in phenylpropanoid and shikimate methods. Shikimic acid is a precursor of aromatic amino acids, numerous alkaloids and indole derivatives. It is create both in free form, and especially in the form of esters (cinnamyl, ethyl, benzyl), in several essential oils, oil of cinnamon, resins and balsams, balsam of Peru and balsm of Tolu etc. These are many significant intermediates in the biosynthetic process of most of the aromatic natural products. These are broadly spread in the plants and have broad range of activities.[32] Furthermore cinnamic acids are too applied as precursor for the synthesis of commercially significant cinnamic esters.[33]

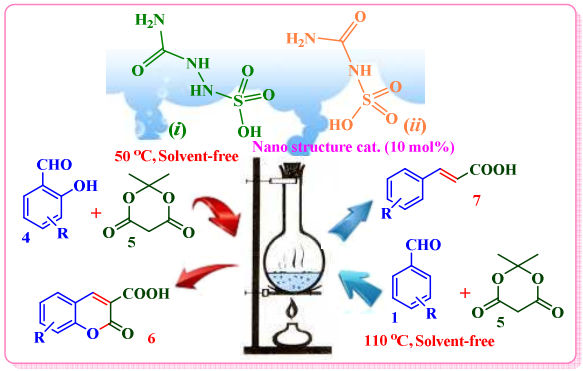
In continuation of our previously studies related to the design, synthesis, applications and development of novel solid acids,[34] *N*-halo reagents,[35] novel nano structure, green and benign ionic liquids, molten salts and organocatalysts for organic functional group transformations,[36] herein, we wish to report synthesis and characterized two biological-based nano organocatalysts with urea moiety. With this aim, semicarbazide hydrochloride and urea have been used for the synthesis of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid respectively (Scheme 1). The synthesized organocatalysts were efficaciously engaged in the synthesis of numerous 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives *via* the condensation reaction of between several aromatic aldehydes and 1-phenyl-3-methylpyrazol-5-one under mild, green and solvent-free conditions (Scheme 2). Moreover, in additional works two organocatalysts were used in the synthesis of several coumarin-3-carboxylic acids *via* the Knoevenagel condensation of Meldrum's acid with salicylaldehyde derivatives and in the synthesis of cinnamic acids by the condensation of Meldrum's acid with aromatic aldehydes under mild, green and solvent-free conditions (Scheme 3).



Scheme 1. The synthesis of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts.



Scheme 2. The synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives using 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts.



Scheme 3. The synthesis of coumarin-3-carboxylic acid and cinnamic acid derivatives using 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts.

Results and discussion

Characterization of 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst (i)

The structure of 2-carbamoylhydrazine-1-sulfonic acid as a novel nano structure organocatalyst was studied and charecterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, CHN, TG, DTG, DTA, EDX, XRD, SEM, TEM, AFM and UV/Vis analysis.

The IR spectrum of the nano organocatalyst showed the two special peaks at 3430 cm^{-1} and 3304 cm^{-1} which can be related to N–H stretching group on semicarbazide moiety and O–H stretching group on –SO_3H. Furthermore, the two peaks at 1207 cm^{-1} and 1172 cm^{-1} are linked to vibrational modes of O–SO_2 bonds. The absorption related to S=O bond vibration appeared at 1043 cm^{-1}. Also, the two peaks at 1686 cm^{-1} and 1609 cm^{-1} are correlated to C=O stretching group on amide moiety respectively (Fig. S1).

Moreover, the ^{1}H NMR and ^{13}C NMR spectra of the 2-carbamoylhydrazine-1-sulfonic acid in DMSO-d_6 are confirmed in Figures S2 and S3, respectively. As Fig. S2, show that, the main peak of ^{1}H NMR spectra of nano

organocatalyst is linked to two –NH group which are detected in δ = 9.35 ppm. The peaks related to $–SO_3H$ group are showed at 8.73 ppm and the peak correlated to $–NH_2$ group on semicarbazide moiety is appeared at 6.59 ppm respectively.

Also, the significant peak of ^{13}C NMR spectra of nano structure organocatalyst is related to the amide group on semicarbazide moiety which is detected at δ = 158.2 ppm (Fig. S3).

The mass spectrum of the catalyst is in accordance with the structure of the catalyst and displayed the parent peak at 155 m/z (Fig. S4). Furthermore, the elemental analysis data (CHNS) to confirm the accuracy of the catalyst with one water molecule.

Thermal gravimetric (TG), derivative thermal gravimetric (DTG) and differential thermal (DTA) analysis of 2-carbamoylhydrazine-1-sulfonic acid were considered at range of 25 to 700 °C, with a temperature increase rate of 10 °C.min^{-1} in a nitrogen atmosphere. The results are shown in Fig. 1. The thermal gravimetric (TG), derivative thermal gravimetric (DTG) and differential thermal (DTA) analysis of the nano structure organocatalyst displayed significance losses in one step, and decomposed after 367 °C.

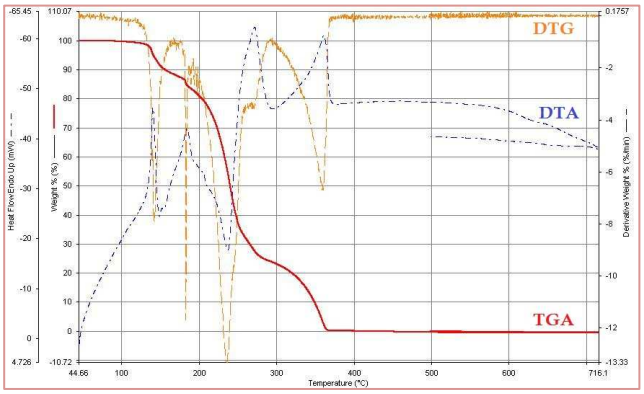


Fig. 1. The thermal gravimetric (TG), derivative thermal gravimetric (DTG) and differential thermal (DTA) analysis of 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Energy-dispersive x-ray spectroscopy (EDX) from the attained nano structure organocatalyst provided the presence of the expected elements in the structure of the organocatalyst, namely oxygen and sulfur (Fig. 2).

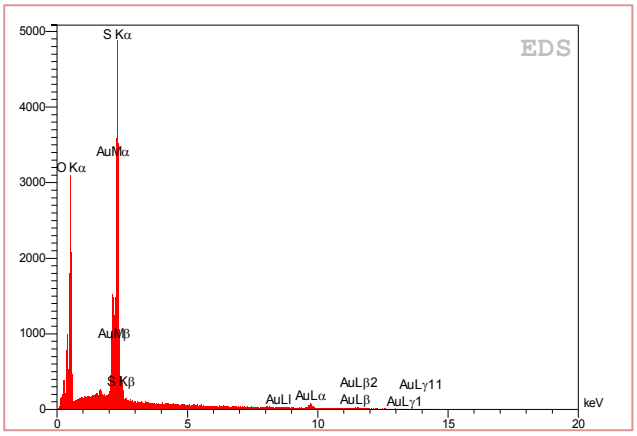


Fig. 2. The energy-dispersive x-ray spectroscopy (EDX) of the 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Size, shape and morphology of 2-carbamoylhydrazine-1-sulfonic acid as the nano structure organocatalyst were studied through x-ray diffraction (XRD) pattern, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis imaging demonstrations. XRD pattern of the organocatalyst was considered in an area of 10-90 degree (Fig. 3). As it is revealed at Fig. 3, XRD pattern displayed diffraction lines of high crystalline nature at 2θ ≈ 16.50°, 20.30°, 21.20°, 23.40°, 25.50°, 26.60°, 27.80°, 28.90°, 31.20°, 36.90°, and 40.20°. Peak width (FWHM), size and inter planar distance linked to XRD pattern of 2-carbamoylhydrazine-1-sulfonic acid were considered in the 16.50° to 36.90° degree and the achieved results have been summarized in Table 1. For instance, assignments for the highest diffraction line 26.60° presented that an FWHM of 0.15 a crystalline size of the catalyst of ca. 54.42 nm by the Scherrer equation [D = Kλ/(βcosθ)] (Where D is the crystalline size, K is the shape factor, being analogous to 0.9 , λ is the x-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle in degree) and an inter planar distance of 0.334710 nm (sing the similar highest diffraction line at 26.60°) was considered *via* the Bragg equation: dhkl = λ/(2sinθ), (λ : Cu radiation (0.154178 nm) were attained. Obtaining crystallite sizes from several diffraction lines by the Scherrer equation were found to be in the nanometer range (27.02-54.42 nm), which is mainly in a good accordance with the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 4).

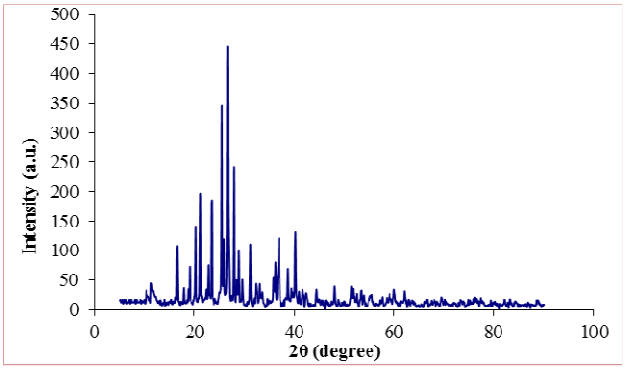


Fig. 3. The x-ray diffraction (XRD) pattern of the 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Table 1. X-ray diffraction (XRD) data for the 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter planar distance [nm]
1	16.50	0.18	44.60	0.536612
2	20.30	0.17	47.47	0.436939
3	21.20	0.19	42.55	0.418590
4	23.40	0.22	36.88	0.379709
5	25.50	0.15	54.30	0.348895

6	26.60	0.15	54.42	0.334710
7	27.80	0.16	51.16	0.320529
8	28.90	0.20	41.02	0.308574
9	31.20	0.19	43.42	0.286331
10	36.90	0.31	27.02	0.243304
11	40.20	0.25	33.84	0.224059

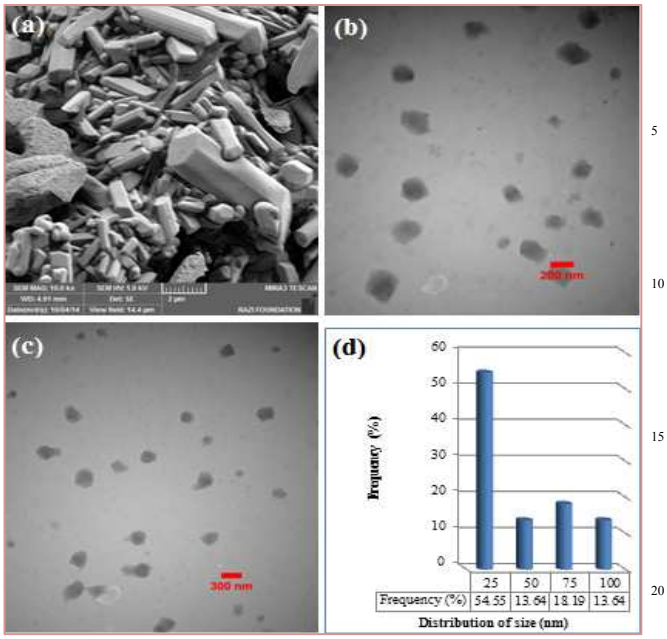


Fig. 4. The scanning electron microscopy (SEM) (a) and transmission electron microscopy (TEM) (b, c and d) of 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Atomic force microscopy (AFM) is a magnificent system that lets us to find and analyze surface make with important resolution and attention. AFM has a gigantic benefit, in that approximately any model can be imaged to be very hard, for example the surface of a ceramic material, or a dispersal of metallic nano composite, or very soft, such as prominently plastic materials, or preferable molecules of proteins. An AFM image gives information about surface morphologies of nano structure organocatalyst through by the two and three dimensions. AFM images were derived with 2.1 μm * 2.1 μm scan part from the images. Fig. 5 show the two and three dimension AFM images of 2-carbamoylhydrazine-1-sulfonic acid nano structure organocatalyst. No key division area in size is identified in the illustrations. From three-dimensional 2.1 μm^2 * 2.1 μm^2 framework, it comes out that the achieved nano structure organocatalyst shows an interrupted structure with a superior beyond planarity. In the surface conformation of the coat, 2-carbamoylhydrazine-1-sulfonic acid nano structure organocatalyst with a size less than 65 nm were detected clearly.

The UV/Vis absorbance spectrum of the nano structure organocatalyst was compared with those of reactants and reaction mixture to highlight the distinction between the UV/Vis absorbance pattern of the catalyst, reactants and reaction mixture. As revealed in Fig. S5, λ_{max} in the UV/Vis spectrum of the organocatalyst showed at about 227 nm. In the UV/Vis spectra of 4-chlorobenzaldehyde, 1-phenyl-3-methylpyrazol-5-one and reaction mixture, nevertheless, the λ_{max} values displayed at about 252, 240 and 244 nm, individually.

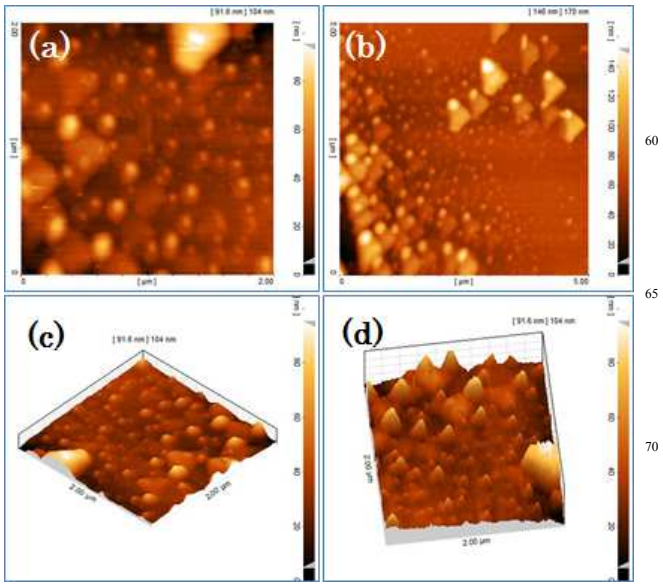


Fig. 5. Two-dimensional (a and b) and three-dimensional (c and d) AFM topography images of 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst.

Characterization of carbamoylsulfamic acid as a nano structure organocatalyst (ii)

The structure of carbamoylsulfamic acid as a nano structure organocatalyst was considered and identified by FT-IR, ^1H NMR, ^{13}C NMR, mass, CHN, TG, DTG, DTA, EDX, XRD, SEM, TEM and UV/Vis analysis.

The IR spectrum of the carbamoylsulfamic acid nano structure organocatalyst presented the two distinct peaks at 3331 cm^{-1} and 3180 cm^{-1} which can be assigned to N–H stretching group on urea moiety and O–H stretching group on $–SO_3H$. Additionally, the two peaks at 1233 cm^{-1} and 1171 cm^{-1} are related to vibrational modes of $O–SO_2$ bonds. The absorption correlated to S=O bond vibration looked at 1024 cm^{-1}. Moreover, the two peaks at 1700 cm^{-1} and 1554 cm^{-1} are correlated to C=O stretching group and C–N stretching group on amide moiety (Fig. S6).

Furthermore, the ^1H NMR and ^{13}C NMR spectra of the carbamoylsulfamic acid in DMSO-d_6 are confirmed in Figures S7 and S8, respectively. As Fig. S7, display that, the key peak of ^1H NMR spectra of nano organocatalyst is related to –NH and $–NH_2$ group which are known in δ = 9.09 ppm and the peaks correlated to $–SO_3H$ group are presented at 7.11 ppm respectively.

Furthermore, the important peak of ^{13}C NMR spectra of nano structure organocatalyst is linked to the amide group on urea moiety which is identified at δ = 154.8 ppm (Fig. S8).

The mass spectrum of the nano structure organocatalyst is in agreement with the structure of the catalyst and showed the parent peak at 140 m/z (Fig. S9). Also, the elemental analysis data (CHNS) to corroborate the definitude of the catalyst with a water molecule.

Thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG) and differential thermal (DTA) analysis of carbamoylsulfamic acid were also considered. The correlated diagrams are presented in Fig. 6. These revealed analysis obviously displayed that the nano structure organocatalyst has good stability; accordingly that there was no clear mass losses before 498 °C. The significant weight loss of the catalyst was occurred after 498 °C, which it can be suitable for the catalytic applications in organic synthesis.

Energy-dispersive x-ray spectroscopy (EDX) from the achieved nano structure organocatalyst provided the existence of the anticipated elements in the structure of the organocatalyst, namely oxygen and sulfur (Fig. 7).

Carbamoylsulfamic acid as a nano structure organocatalyst was studied by x-ray diffraction (XRD) pattern (Fig. 8), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 18). In this attention, to corroborate the structure of carbamoylsulfamic acid, firstly, its XRD pattern was considered. As revealed in Fig. 8, the XRD patterns of nano structure organocatalyst display peaks at 2θ ≈ 15.70°, 21.50°, 23.20°, 24.70°, 30.10°, 34.10° and 41.80°, correspondingly, this was confirmed through the described value of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 9). Peak width (FWHM), size and inter planar distance linked to XRD pattern of nano structure organocatalyst were considered in the 16.00° to 32.40° degree and the achieved results have been summarized in Table 2. The average crystallite size D was calculated by the Debye–Scherrer formula: $D = K\lambda/(\beta\cos\theta)$, K is the Scherrer constant, λ being the x-ray wavelength, β is the half-maximum peak width, and θ is the Bragg diffraction angle. The average size of the nano structure organocatalyst, subsequently, attained from this equation was found to be about 9.01-63.92 nm, which is basically in a good agreement with the scanning electron microscopy and transmission electron microscopy (Fig. 9).

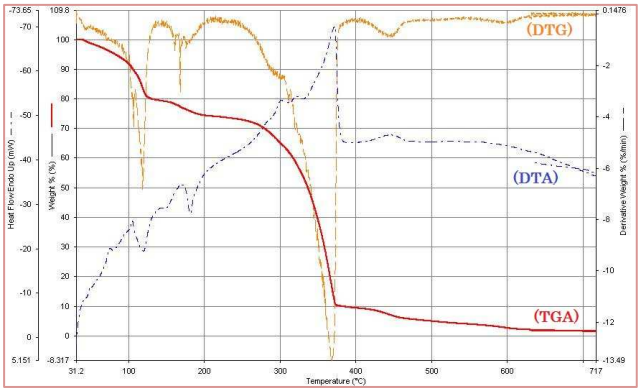


Fig. 6. The thermal gravimetric (TG), derivative thermal gravimetric (DTG) and differential thermal (DTA) analysis of carbamoylsulfamic acid as a nano structure organocatalyst.

The UV/Vis absorbance spectrum of the nano structure organocatalyst was compared with those of reactants, reaction mixture and product to highlight the diversity between the UV/Vis absorbance pattern of the catalyst, reactants, reaction mixture and product. As displayed in Fig. S10, λ_{max} in the UV/Vis spectrum of the organocatalyst presented at about 233 nm. In the UV/Vis spectra of 4-chlorobenzaldehyde, 1-phenyl-3-methylpyrazol-5-one, reaction mixture and product, however, the λ_{max} values presented at about 252, 240, 229 and 245 nm, respectively.

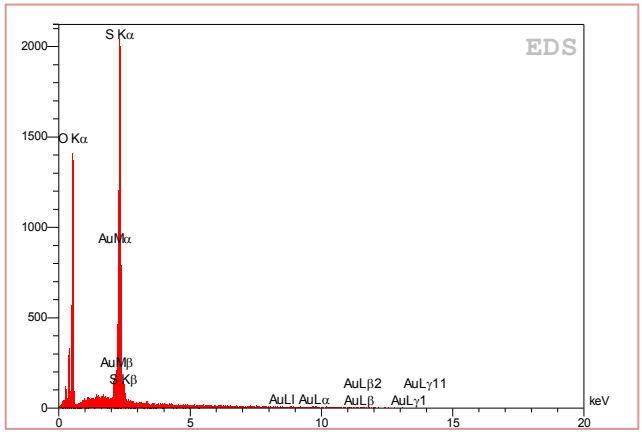


Fig. 7. The energy-dispersive x-ray spectroscopy (EDX) of the carbamoylsulfamic acid as a nano structure organocatalyst.

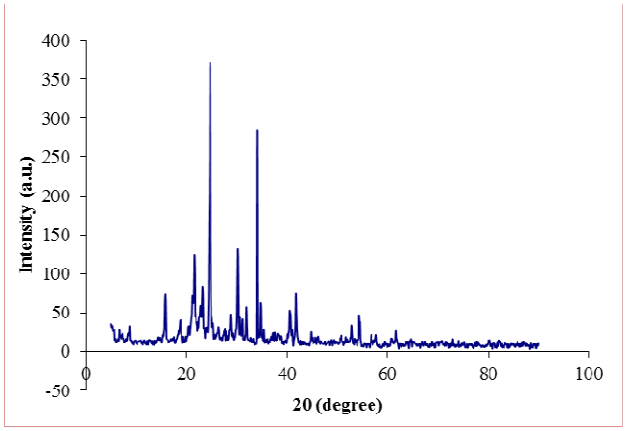


Fig. 8. The x-ray diffraction (XRD) pattern of the carbamoylsulfamic acid as a nano structure organocatalyst.

Table 2. X-ray diffraction (XRD) data for the carbamoylsulfamic acid as a nano structure organocatalyst.

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter planar distance [nm]
1	15.70	0.32	36.45	0.563772
2	21.50	0.63	12.84	0.414817
3	23.20	0.90	9.01	0.390921
4	24.70	0.25	32.53	0.360010
5	30.10	0.30	27.71	0.296539
6	34.10	0.13	63.92	0.262614
7	41.80	0.40	21.26	0.215845

Application of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts in the synthesis of 4,4'-(arylmethylene)bis(1H-pyrazol-5-ol) derivatives.

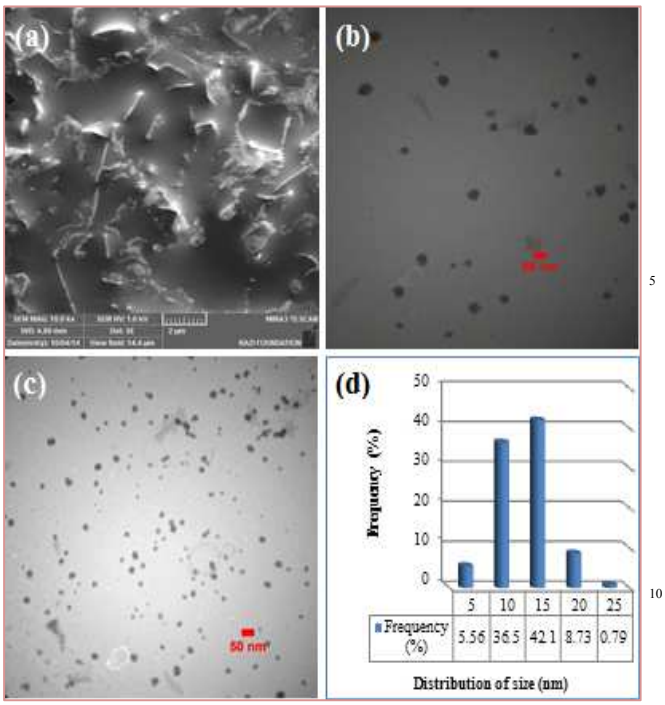


Fig. 9. The scanning electron microscopy (SEM) (a) and transmission electron microscopy (TEM) (b, c and d) of carbamoylsulfamic acid as a nano structure organocatalyst.

At first, to optimize the reaction conditions, the condensation reaction of 4-chlorobenzaldehyde and 1-phenyl-3-methylpyrazol-5-one was chosen as a model and various amounts of nano organocatalysts at range of 50-90 °C were confirmed on it under solvent-free conditions (Table 3). As revealed in Table 3, the best results were achieved when the reaction was attained in the presence of 10 mol% of nano structure organocatalyst at 60 °C (Table 3, entry 3). No improvement was observed in the yield of reaction through increasing the amount of the nano organocatalysts and the temperature (Table 3, entries 4-12). Table 3 obviously displays that in the absence of nano organocatalysts, the product formed in low yields. To compare the effect of the solution in comparison with solvent-free conditions, a mixture of 4-chlorobenzaldehyde and 1-phenyl-3-methylpyrazol-5-one as model reaction, in the presence of 10 mol% of nano organocatalysts in several solvents such as C_2H_5OH, CH_3CN, CH_3CO_2Et and toluene were studied at 60 °C. Solvent-free condition was the best condition in this reaction.

Table 3. Result of amount of the catalyst and temperature on the condensation reaction of 4-chlorobenzaldehyde and 1-phenyl-3-methylpyrazol-5-one under solvent-free conditions.

Entry	Catalyst amount (mol%)	Reaction temperature (°C)	Reaction time (min)		Yield (%)	
			Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)
1	—	60	160	160	60	60
2	10	50	25	30	87	85
3	10	60	15	20	91	93
4	10	70	20	20	90	90
5	10	80	20	20	92	90
6	10	90	20	20	92	90
7	15	50	25	30	87	85
8	20	50	25	30	87	85
9	15	60	15	20	91	93
10	20	60	15	20	91	93
11	15	70	20	20	90	90
12	20	70	20	20	90	90

After optimization of the reaction conditions, to study the efficacy and the scope of the offered process, several of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives were produced *via* the condensation reaction between aromatic aldehydes and 1-phenyl-3-methylpyrazol-5-one in the presence of catalytic amounts of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts under solvent-free reaction conditions. The results have been represented in Table 4.

The effect of substituents on the aromatic ring was estimated strong effects in terms of yields under these reaction conditions. Both class of aromatic aldehydes including electron-releasing, electron-withdrawing substituents on their aromatic ring offered the favorable products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes having electron withdrawing groups were rather faster than electron donating groups.

Table 4. Synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives using 10 mol% of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as a nano structure organocatalyst.

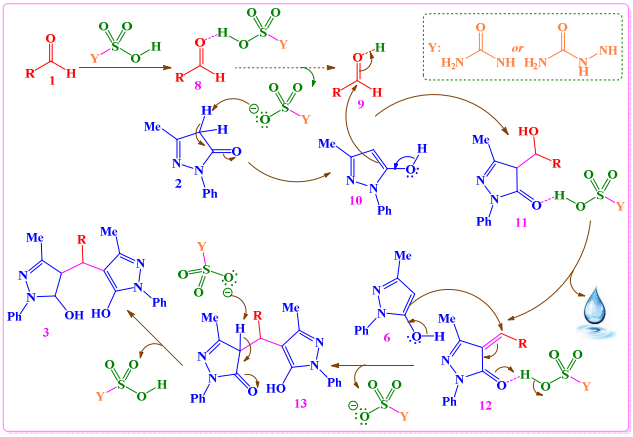
Entry	Aldehyde	Time (min)		Yield (%)		M.p (°C) [Lit.][Ref.]
		Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)	
1	*N*,*N*-Dimethylaminobenzaldehyde	210	210	87	85	172-173
2	4-Chloro-3-nitrobenzaldehyde	20	20	95	92	238-240 [237-238][37]
3	3-Bromobenzaldehyde	15	12	96	98	172-174 [173-176][38]
4	Terephthalaldehyde (2:1)	30	25	90	87	211-213

5	Terephthalaldehyde	40	40	83	85	213-215 [194-196][39]
6	Terephthalaldehyde-mono-diethylacetal	60	50	89	85	254-255
7	3-Fluorobenzaldehyde	30	25	97	96	183-184
8	Ethyl-3-formyl-1*H*-indol-2-carbaldehyde	30	30	90	93	231-233
9	4-Pyridinecarboxaldehyde	20	20	94	93	248-250
10	4-Chlorobenzaldehyde	15	20	91	93	213-214 [215-216][37]
11	2-Chlorobenzaldehyde	12	15	95	94	236-237 [235-237][37]
12	2,4-Dichlorobenzaldehyde	25	30	90	85	229-230 [227-229][37]
13	3-Chlorobenzaldehyde	15	15	92	94	235-237 [150-152][39]
14	2-Methoxybenzaldehyde	40	45	88	90	212-213 [210-213][37]
15	3-Hydroxybenzaldehyde	30	30	93	94	166-168 [165-168][40]
16	Benzaldeyhe	20	20	95	93	161-163 [169-171][37]
17	3-Nitrobenzaldehyde	15	20	97	94	150-151 [151-154][37]
18	4-Nitrobenzaldehyde	10	10	98	95	230-232 [225][37]
19	3-Phenoxybenzaldehyde	25	30	94	97	194-195
20	α-Methylcinnamaldehyde	45	55	90	92	163-164
21	2-Hydroxybenzaldehyde	30	30	93	90	227-228 [227-229][41]
22	Naphthalene-2-carbaldehyde	27	35	95	90	206-207 [204-206][37]
23	Naphthalene-1-carbaldehyde	45	45	98	99	213-215 [228-230][38]
24	4-Hydroxy-3-methoxybenzaldehyde	45	50	91	94	205-207 [200-201][42]
25	2-Nitrobenzaldehyde	30	30	90	92	222-224 [221-223][39]
26	4-Bromobenzaldehyde	10	10	96	94	202-204 [183-185][37]
27	4-Fluorobenzaldehyde	20	25	95	97	145-146 [182-184][37]

We offer the probable mechanism to explanation for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives **3**. Initial step includes the creation of benzylidene intermediaite **8** *via* the nucleophilic addition of 1-phenyl-3-methyl-5-pyrazolone **2** to aromatic aldehyde **1** followed through dehydration. Then, the second molecule of 1-phenyl-3-methyl-5-pyrazolone **2** adds in the Michael addition approach to give 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives **3** (Scheme 3).

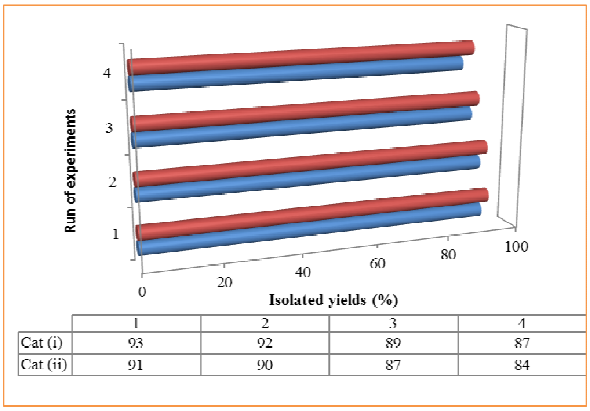
Additionally, recycle and reusability of the catalysts were also examined upon the condensation between 4-chlorobenzaldehyde and 1-phenyl-3-methylpyrazol-5-one. After the completion of the reaction, ethyl acetate was added to the reaction mixture and stirred and heated to separate product and remained starting materials from the catalyst. This solution was washed with absolute ethanol to separate organocatalysts from other materials (the product and starting materials are soluble in hot ethyl acetate and nano organocatalysts are soluble in absolute ethanol). Furthermore, organocatalysts were separated and reused for alternative reaction after removing of ethanol. The catalytic activities of the catalysts were restored within the limits of the experimental errors for four continuous runs (Fig. 10). The structure of reused organocatalysts was also confident *via* IR spectra and after its application in the reaction. Furthermore, the size and morphology of reused catalysts was studied by XRD pattern (Figures S11 and S12).

To study the efficacy of our organocatalysts (*via* the calculate of TOF, TON and atomic economic values) on the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives, the condensation of 4-chlorobenzaldehyde and 1-phenyl-3-methylpyrazol-5-one was used as a model. The TOF values were calculated *via* the equation TOF = Yield (%)/[Time (min)×Catalyst amount (mol%)]. TON values were calculated *via* the equation TOF = Yield (%)/Catalyst amount (mol%). Atomic economic values were calculated *via* the equation AE = [molecular weight/The total molecular weight]×100. In the presence of cat (*i*) the TOF values, 0.47 was measured and using cat (*ii*) the TOF values, 0.61 was measured. In the presence of cat (*i*) the TON values, 9.3 was measured and using cat (*ii*) the TON values, 9.1 was measured. In the presence of cat (*i*) or cat (*ii*) the atomic economic values, 96.32 was measured (Table 5).



Scheme 3. Suggested mechanism for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives using 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts.

Application of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts in the synthesis of coumarin-3-carboxylic acid.



	1	2	3	4
Cat (i)	93	92	89	87
Cat (ii)	91	90	87	84

Fig. 10. The recycle and reusability of the nano structure organocatalyst (*i*) in 20 minutes and nano structure organocatalyst (*ii*) in 15 minutes.

Initially, to optimize the reaction conditions, the condensation reaction of salicylaldehyde with Meldrum's acid was selected as a model and different amounts of nano organocatalysts at range of 25-70 °C were confirmed on it under solvent-free conditions (Table 6). As shown in Table 6, the best results were attained when the reaction was achieved using 10 mol% of nano structure organocatalyst at 50 °C (Table 6, entry 3). No betterment was detected in the yield of reaction by increasing the amount of the nano organocatalysts and the temperature (Table 6, entries 4-7). Table 6 clearly exhibitions that using nano organocatalysts, the product syntheized in low yields. To compare the effect of the solution in comparison with solvent-free conditions, a mixture of salicylaldehyde and Meldrum's acid as typical reaction, in the presence of 10 mol% of nano organocatalysts in numerous solvents for example C_2H_5OH, CH_3CN, CH_3CO_2Et and toluene were studied at 50 °C. Solvent-free condition was the best condition in this reaction.

Table 5. TOF and TON of nano organocataylsts after recycling.

Recycle	TOF		TON	
	Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)
1	0.61	0.47	9.1	9.3
2	0.59	0.43	8.8	8.5
3	0.53	0.30	8.0	6.0
4	0.49	0.26	7.3	5.1

Table 6. Result of amount of the catalyst and temperature in the condensation reaction between salicylaldehyde and Meldrum's acid under solvent-free conditions.

Entry	Catalyst amount (mol%)	Reaction temperature (°C)	Reaction time (min)		Yield (%)	
			Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)
1	5	50	20	30	91	94
2	10	r.t.	180	180	70	72
3	10	50	5	15	97	98
4	10	60	5	15	97	98
5	10	70	5	15	97	98
6	15	50	5	15	96	96
7	20	50	5	15	96	96

Subsequently optimization of the reaction conditions, to study the efficiency and the scope of the introduced procedure, numerous of coumarin-3-carboxylic acid derivatives were formed *via* the Knoevenagel condensation reaction between several salicylaldehyde with Meldrum's acid using catalytic amounts of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts under solvent-free reaction conditions. The results possess revealed in Table 7. The effect of substituents on the aromatic ring was evaluated strong effects in terms of yields under these reaction conditions. Both class of aromatic salicylaldehydes counting electron-releasing, electron-withdrawing substituents on their aromatic ring introduced the appropriate products in high to excellent yields in short reaction times. The reaction times of aromatic salicylaldehydes having electron withdrawing groups were rather faster than electron donating groups. In addition, recycle and reusability of the catalysts were also examined on the condensation of salicylaldehyde with Meldrum's acid. Similarly, organocatalysts were separated and reused for alternative reaction after removing of ethanol.

Table 7. Synthesis of coumarin-3-carboxylic acid derivatives *via* the Knoevenagel condensation using 10 mol% of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as a nano structure organocatalyst.

Entry	Salicylaldehyde	Time (min)		Yield (%)		M.p (°C)[Ref.]
		Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)	
1	Salicylaldehyde	5	15	87	98	190-192[43]
2	5-Bromosalicylaldehyde	20	30	94	95	196-198[43]
3	2-Hydroxy-1-naphthaldehyde	40	50	95	96	183-185[43]
4	5-Nitrosalicylaldehyde	15	20	97	85	216-217[43]
5	5-Hydroxysalicylaldehyde	5	15	96	88	268-270[44]
6	3-Hydroxysalicylaldehyde	40	30	95	83	284-286
7	3,5-Dichlorosalicylaldehyde	20	25	94	96	193-195[44]

Application of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts in the synthesis of cinnamic acid.

At first, to optimize the reaction conditions, the condensation reaction between benzaldehydes with Meldrum's acid was selected as a typical and various amounts of nano organocatalysts at range of 25-110 °C were confirmed upon it under solvent-free conditions (Table 8). As revealed in Table 8, the appropriate results were achieved when the reaction was attained using 10 mol% of nano structure organocatalyst at 110 °C (Table 8, entry 6). No improvement was identified in the yield of reaction through increasing the amount of the nano organocatalysts and the temperature (Table 8, entries 7 and 8). Table 8 obviously shows that in the presence of nano

organocatalysts, the product prepared in low yields. To compare the effect of the solution in comparison with solvent-free conditions, a mixture of benzaldehye and Meldrum's acid as model reaction, using 10 mol% of nano organocatalysts in various solvents such as C_2H_5OH, CH_3CN, CH_3CO_2Et and toluene were considered at 110 °C. Solvent-free condition was the best condition in this reaction.

Table 8. Result of amount of the catalyst and temperature in the condensation reaction of benzaldehyde and Meldrum's acid under solvent-free conditions.

Entry	Catalyst amount (mol%)	Reaction temperature (°C)	Reaction time (min)		Yield (%)	
			Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)
1	5	110	45	60	91	93
2	10	r.t.	180	180	50	50
3	10	60	180	180	75	75
4	10	90	120	120	96	94
5	10	100	60	60	95	96
6	10	110	20	25	97	98
7	15	110	20	25	96	97
8	20	110	20	25	95	92

Afterwards optimization of the reaction conditions, to study the performance and the scope of the presented process, several of cinnamic acid derivatives were synthesized *via* the condensation reaction between various aromatic aldehyde with Meldrum's acid in the presence of catalytic amounts of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts under solvent-free reaction conditions. The results have shown in Table 9. The effect of substituents on the aromatic ring was estimated strong effects in terms of yields under these reaction conditions. Both class of aromatic aldehydes containing electron-releasing, electron-withdrawing substituents on their aromatic ring presented the applicable products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes having electron withdrawing groups were rather faster than electron donating groups. Moreover, recycle and reusability of the catalysts were also studied on the condensation of benzaldehyde with Meldrum's acid. Likewise, organocatalysts were separated and reused for alternative reaction after removing of ethanol.

Table 9. Synthesis of cinnamic acid derivatives using 10 mol% of 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as a nano structure organocatalyst.

Entry	Aldehyde	Time (min)		Yield (%)		M.p (°C)[Ref.]
		Cat (*ii*)	Cat (*i*)	Cat (*ii*)	Cat (*i*)	
1	Benzaldehyde	20	25	97	98	128-129[45]
2	4-Chlorobenzaldehyde	5	10	94	94	254-256[45]
3	2-Chlorobenzaldehyde	10	20	95	96	209-210
4	2,4-Dichlorobenzaldehyde	5	8	98	98	235-238
5	4-Nitrobenzaldehyde	5	10	93	95	292[dec-46]
6	4-Chloro-3-nitrobenzaldehyde	15	20	95	93	187-189
7	3-Nitrobenzaldehyde	10	15	92	92	202-203[45]
8	Naphthalene-1-carbaldehyde	5	8	96	95	215-217
9	3-Bromobenzaldehyde	10	12	94	93	174-175
10	4-Methoxybenzaldehyde	20	25	93	96	168-170[45]
11	2-Methoxybenzaldehyde	30	40	91	94	183-185[47]
12	4-Methylbenzaldehyde	30	30	95	94	200-202[46]
13	Terephthalaldehyde	10	10	90	89	187[dec]

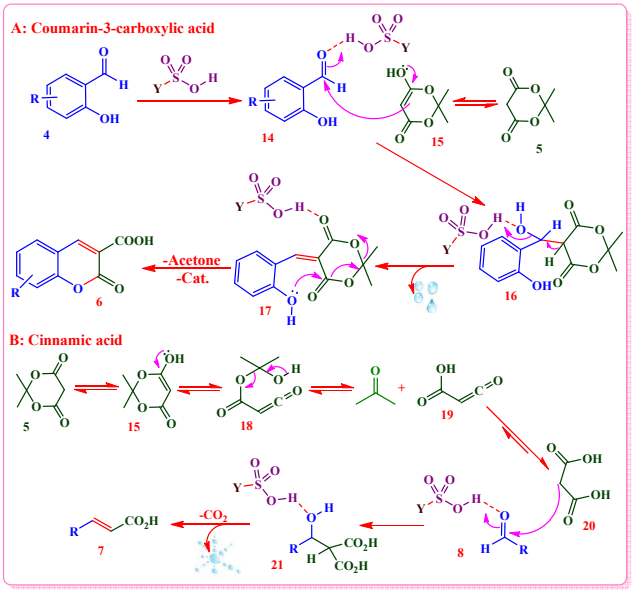
A probable mechanism for the synthesis of coumarin-3-carboxylic acids and cinnamic acids are suggested in Scheme 4.[43, 45] A possible reaction mechanism with a knoevenagel reaction between salicylaldehyde derivatives (**4**) with Meldrum's acid (**5**) in the presence of catalytic amounts of 2-carbamoylhydrazine-1-sulfonic acid or carbamoylsulfamic acid to give adduct (**17**) followed by a nucleophilic attack of the phenolic group on the carbonyl group of Meldrum's acid. This resulted in the opening of Meldrum's acid ring and preparing of coumarin-3-carboxylic acid derivatives (**6**). Also, Meldrum's acid has $pK_a = 5$ and because it is sensitive to heat, decyclization happens at high temperatures according to the proposed mechanism.[48] Initial step contains the formation of intermediate (**21**) *via* the nucleophilic addition of Meldrum's acid with open ring (**20**) to aromatic aldehyde (**8**). Finally, the removing of one water molecule leads to synthesis of cinnamic acids (**7**).

To compare the efficacy of our catalyst with some studied catalysts for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives, we have presented the results of these catalysts to achieve the condensation of 4-nitrobenzaldehyde with 1-phenyl-3-methyl-5-pyrazolone (in the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol)), Meldrum's acid with salicylaldehyde (in the synthesis of coumarin-3-carboxylic acid) and benzaldehyde with Meldrum's acid (in the synthesis of cinnamic acid) in Table 10. As Table 10 shows, the nano structure organo catalysts has remarkably improved the synthesis of products in different terms.

Conclusion

In summary, two novel, mild, green and efficient nano structure organo solid acids namely 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid with urea as a biological moiety were designed, synthesized and completely identified by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, elemental analysis,

thermal gravimetric (TG), derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX), atomic force microscopy (AFM) and UV/Vis analysis. Catalytic applications of described organo solid acids were investigated on the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives *via* the condensation reaction of between several aromatic aldehydes and 1-phenyl-3-methylpyrazol-5-one (synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols)), the Knoevenagel condensation of Meldrum's acid with salicylaldehyde derivatives (synthesis of coumarin-3-carboxylic acids) and the condensation of Meldrum's acid with aromatic aldehydes (synthesis of cinnamic acids) under mild, green and solvent-free conditions. Further studies showed that the nano structure organocatalysts acidity plays a major role in the dual-catalyzed reactions. Significant advantages of this study are relatively environmentally benign, biological-based catalysts, low cost, cleaner reaction profile, high yield, short reaction time, simplicity of product isolation, recycle and reusability of the nano organocatalysts and close agreement with the green chemistry disciplines. Finally, on the basis of our observations and the above mentioned advantages, herein, we thought that both of the described biological-based acids and/or catalysts have potential for industrial production.



Scheme 4. Proposed mechanism for the synthesis of coumarin-3-carboxylic acids and cinnamic acids using 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid as nano structure organocatalysts.

Table 10. Comparison of the results in the synthesis of model product using nano organo catalyst with those obtained by the reported catalysts.

Entry	Reaction condition	Catalyst loading	Time (min)	Yield (%)	Ref.
1	Cat (*i*), Solvent-free, 60 °C	10 mol%	20	93	This work
2	Cat (*ii*), Solvent-free, 60 °C	10 mol%	15	91	This work
3	[Dsim]$AlCl_4$, solvent-free, 90 °C	1 mol%	40	91	36e
4	Silica-bonded S-sulfonic acid (SBSSA), EtOH, reflux condition	18 mol%	40	90	40
5	PEG-400, 110 °C	282 mol%	60	94	49
6	Poly(ethylene glycol)-bound sulfonic acid (PEG-SO_3H), water, reflux condition	1.5 mol%	15	93	39
7	Cat (*i*), Solvent-free, 50 °C	10 mol%	15	95	This work
8	Cat (*ii*), Solvent-free, 50 °C	10 mol%	5	87	This work
9	Silica sulfuric acid, 120	0.02g	45	90	50
10	$SnCl_2.2H_2O$, Solvent-free, 80 °C	10 mol%	60	80	43
11	K_3PO_4, C_2H_5OH, r.t.	20 mol%	45	94	44
12	Cat (*i*), Solvent-free, 110 °C	10 mol%	25	98	This work
13	Cat (*ii*), Solvent-free, 110 °C	10 mol%	20	97	This work
14	Piperidine, C_2H_5OH (200 mL), 100 °C	1.5 mmol	7 h	80	51
15	BBr_3, 4-DMAP, Py	—	12 h	65	45

Experimental

General procedure for the preparation of nano structure organocatalyst: 2-carbamoylhydrazine-1-sulfonic acid.

In a round-bottomed flask (50 mL) counting semicarbazide hydrochloride (10 mmol; 1.115 g) in CH_2Cl_2 (3 mL), was drop wise added Chlorosulfonic acid (10 mmol; 1.165 g) and stirred at 0-25 °C for 60 minutes. Then, the solvent was removed through distillation under reduced pressure and the product was dried under vacuum at 50 °C for 60 minutes. The white solid product was filtered, washed with CH_2Cl_2 for three times, and then dried under vacuum conditions. 2-Carbamoylhydrazine-1-sulfonic acid was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, elemental analysis, thermal gravimetric (TG), derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX) and atomic force microscopy (AFM) analysis (Scheme 1).

2-Carbamoylhydrazine-1-sulfonic acid: M.p: 142-144 °C; Yield: 98% (1.520 g); Spectral data: IR (KBr): υ 3430,

3300, 3096, 1608, 1564, 1491, 1206, 1169, 1042, 881 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 6.59 (brs, 2H, —NH_2), 8.73 (brs, 1H, —OH), 9.35 (brs, 2H, —NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.2; MS: m/z = 155 $[M]^+$; Anal. Calcd for $CH_5N_3O_4S + H_2O$: C, 6.82; H, 3.12; N, 23.34; S, 19.21. found: C, 6.94; H, 4.08; N, 24.27; S, 18.52.

General procedure for the preparation of nano structure organocatalyst: carbamoylsulfamic acid.

In a round-bottomed flask (50 mL) counting urea (10 mmol; 0.600 g) in CH_2Cl_2 (3 mL), was drop wise added Chlorosulfonic acid (10 mmol; 1.165 g) and stirred at 0-25 °C for 60 minutes. Then, the solvent was removed through distillation under reduced pressure and the product was dried under vacuum at 50 °C for 60 minutes. The white solid product was filtered, washed with CH_2Cl_2 for three times, and then dried under vacuum conditions. Carbamoylsulfamic acid was characterized by FT-IR, ^1H NMR, ^{13}C NMR, mass, elemental analysis, thermal gravimetric (TG), derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDX) analysis (Scheme 1).

Carbamoylsulfamic acid: M.p: 102-104 °C; Yield: 98% (1.373 g); Spectral data: IR (KBr): υ 3331, 3180, 1700, 1554, 1316, 1233, 1171, 1057, 1024, 883 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.11 (brs, 1H, —OH), 8.73 (brs, 1H, —NH and —NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8; MS: m/z = 140 $[M]^+$; Anal. Calcd for $CH_4N_2O_4S + H_2O$: C, 7.82; H, 3.32; N, 17.49; S, 21.38. found: C, 7.60; H, 3.82; N, 17.72; S, 20.27.

General procedure for the preparation of 4,4'-(arylmethylene)bis(1H-pyrazol-5-ol) derivatives.

To the mixture of aromatic aldehyde (1 mmol) and 1-phenyl-3-methyl-5-pyrazolone (2 mmol) and 2-carbamoylhydrazine-1-sulfonic acid or carbamoylsulfamic acid as nano structure organocatalysts (10 mol%) was added and mixed under solvent-free conditions at 60 °C for the appropriate time described in Table 4. After completion of the reaction which was observed *via* TLC (*n*-hexane/ethyl acetate: 5/2), the mixture washed with water and separated of nano organocatalyst, the solid product purified by recrystallization from ethanol. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds.

General procedure for the preparation of coumarin-3-carboxylic acid derivatives.

To a mixture of Meldrum's acid (1 mmol) with salicylaldehyde derivatives (1 mmol) and 2-carbamoylhydrazine-1-sulfonic acid or carbamoylsulfamic acid as nano structure organocatalysts (10 mol%) was added and mixed under solvent-free conditions at 50 °C for the appropriate time described in Table 7. After completion of the reaction which was detected *via* TLC (*n*-hexane/ethyl acetate: 5/3), the mixture washed with water and separated of nano organocatalyst, the solid product purified by recrystallization from ethanol. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds.

General procedure for the preparation of cinnamic acid derivatives.

To a mixture of Meldrum's acid (1 mmol) with aromatic aldehydes (1 mmol) and 2-carbamoylhydrazine-1-sulfonic acid or carbamoylsulfamic acid as nano structure organocatalysts (10 mol%) was added and mixed under solvent-free conditions at 110 °C for the suitable time described in Table 9. After completion of the reaction which was identified *via* TLC (*n*-hexane/ethyl acetate: 5/3), the mixture washed with water and separated of nano organocatalyst, the solid product purified by recrystallization from ethanol. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds.

Spectral data analysis for compounds

4-((4-(Dimethylamino)phenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 1): Yellow solid; m.p. 172-173; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.30 (s, 6H), 2.82 (s, 6H), 4.84 (s, 1H, CH), 6.65 (d, 2H), 7.06 (d, 2H), 7.24 (t, 2H), 7.44 (t, 4H), 7.71 (d, 4H), 12.32 (s, 1H, OH), 13.96 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.11, 32.69, 40.85, 113.01, 120.91, 125.94, 128.09, 129.37, 130.43, 138.10, 146.64, 149.28, 157.92; IR (KBr, cm-1): 3460, 3075, 1600, 1582, 1517, 1502, 1481, 1398, 1348, 1282, 1199, 1042, 810, 748, 690; m/z (%)= 480 (M+).

4,4'-((4-(Diethoxymethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 6): Dark violet powder; m.p. 254-255; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.36 (s, 6H), 2.33 (m, 6H), 3.38 (4H), 4.88 (s, 1H), 5.07 (s, 1H), 7.22 (m, 7H), 7.44 (m, 2H), 7.69 (m, 2H), 7.87 (m, 3H), 12.47 (s, 1H, OH), 14.07 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.09, 13.57, 33.23, 58.23, 118.77, 118.89, 121.11, 125.25, 126.14, 127.45, 128.51, 128.82, 129.34, 129.406, 130.00, 133.68, 134.23, 134.84, 136.79, 138.44, 140.45, 146.68, 146.75, 149.92, 152.24 ; IR (KBr, cm-1): 3473,3063, 2909, 1616, 1561, 1502, 1499, 1457, 1399, 1368, 1315, 1212, 1119, 995, 855, 811, 747, 687; m/z (%)= 538 (M+).

4-((3-Fluorophenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (table 4, entry 7): Cream solid; m.p. 183-184, ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.33 (s, 6H), 4.97 (s, 1H), 7.10 (m, 2H), 7.27 (m, 4H), 7.44 (t, 4H), 7.71 (q, 4H), 12.55 (s, 1H, OH), 13.94 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.06, 32.89, 115.10, 115.31, 121.02, 126.08, 129.12, 129.39, 129.45, 129.53, 137.76, 138.63, 138.65, 146.67, 159.93, 162.33; IR (KBr, cm-1): 3444, 3068, 2983, 2930, 1602, 1578, 1503, 1408, 1374, 1347, 1284, 1284, 1216, 1156, 1025, 905, 841, 812, 738, 749, 688; m/z (%)= 454 (M+).

Ethyl 3-(bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-1H-indole-2-carboxylate (Table 4, entry 8): Pale yellow solid; m.p. 231-233, ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.36 (t, 3H), 2.19(s, 6H), 4.38 (q, 2H), 5.33 (s, 1H, CH) 6.93 (t, 1H), 7.20 (m, 3H), 7.42 (q,

5H), 7.69 (d, 4H), 7.97 (s, 1H), 12.25 (s, 1H, OH), 13.96(s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.32, 14.76,32.64, 60.86,112.68, 119.66, 120.91, 122.33, 123.39, 124.81, 125.81, 126.80, 129.36, 136.72, 147.54, 153.62, 162.26; IR (KBr, cm-1): 3456, 3061, 2924, 2884, 1709, 1622, 1603, 1551, 1497, 1456, 1398, 1319, 1260, 1182, 1151, 1096, 1030, 835, 785, 742, 689; m/z (%)= 548 (M+).

4,4'-(Pyridin-4-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 9): Dark violet solid; m.p. 248-250, ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.29 (s, 6H), 5.29 (s, 1H, CH), 7.09 (t, 2H), 7.36 (t, 4H), 7.80 (s, 2H), 7.91 (d, 4H),8.82 (s, 2H), 12.33 (s, 1H, OH), 13.79 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 15.92, 32.89, 111.65, 118.46, 121.16, 123.93, 129.06, 129.45, 139.64, 145.19, 149.45, 162.59; IR (KBr, cm-1): 3352, 3087, 2983, 1651, 1634, 1593, 1481, 1319, 1163, 999, 813, 768; m/z (%)= 435 (M+).

4-((3-Hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)(3-phenoxyphenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 19): Cream solid; m.p. 194-195; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.31 (s, 6H), 4.99 (s, 1H, CH), 6.79 (d, 1H), 7.02 (m, 5H), 7.28 (m, 5H), 7.44 (t, 4H), 7.68 (d, 4H),12.50 (s, 1H, OH) 13.98 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.01, 33.32,116.28, 117.99, 118.86, 121.06, 122.88, 123.73, 126.15, 129.40, 130.13, 130.35, 137.63, 144.90, 146.74, 156.80, 156.85; IR (KBr, cm-1): 3434, 3070, 2923, 1598, 1578, 1498, 1439, 1371, 1253, 1224, 1161, 1019, 787, 752, 685; m/z (%)= 529 (M+).

4-(1-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-methyl-3-phenylallyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 20): Pale yellow solid; m.p. 163-164; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.79 (s, 3H), 2.29(s, 6H), 4.33 (s, 1H, CH), 6.36 (s, 1H), 7.25 (m, 6H), 7.44 (t, 4H), 7.72 (d, 4H), 12.39 (s, 1H, OH), 13.89 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 12.05, 17.89, 37.51, 84.28, 121.02, 124.74, 125.97, 126.50, 128.56, 129.22, 129.39, 137.46, 138.44, 146.89, 157.03; IR (KBr, cm-1): 3435, 3058, 2921, 1602, 1579, 1500, 1379, 1266, 1188, 1023, 852, 793, 751, 688; m/z (%)= 476 (M+).

4-((4-Hydroxy-3-methoxyphenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 24): Yellow solid; m.p. 205-207; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.30 (s, 6H), 3.66 (s, 3H), 4.84 (s, 1H, CH), 6.67 (t, 2H), 6.84 (s, 1H), 7.24 (t, 2H), 7.44 (t, 4H), 7.70 (d, 4H), 8.77 (s, 1H), 12.42 (s, 1H, OH), 14.01 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ (ppm) 13.01, 33.31, 56.11, 112.38, 115.61, 120.08, 121.03, 126.01, 129.39, 133.73, 145.32, 146.61, 147.63, 154.33; IR (KBr, cm-1): 3456, 3172, 2923, 1600, 1579, 1499, 1415, 1265, 1126, 1039, 782, 752, 692; m/z (%)= 481 (M+).

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Notes and references

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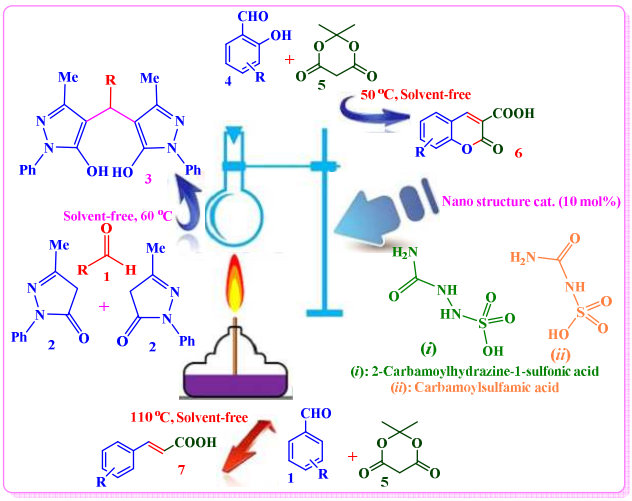
Abstract

Synthesis and characterization of two novel biological-based nano organo solid acids with urea moiety and their catalytic applications in the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions



Mohammad Ali Zolfigol,* Roya Ayazi-Nasrabadi and Saeed Baghery

A benign green and straight-forward synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives using nano structure organocatalysts namely 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid has been developed.

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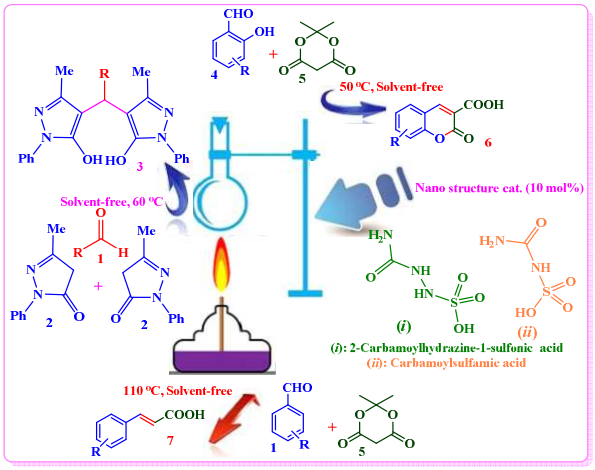
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

Graphycal Abstract

Synthesis and characterization of two novel biological-based nano organo solid acids with urea moiety and their catalytic applications in the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions



Mohammad Ali Zolfigol,* Roya Ayazi-Nasrabadi, Saeed Baghery

A benign green and straight-forward synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ol) derivatives using nano structure organocatalysts namely 2-carbamoylhydrazine-1-sulfonic acid and carbamoylsulfamic acid has been developed.