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ARTICLE TYPE

Nano–ZrO_2 sulfuric acid: A heterogeneous solid acid nano catalyst for Biginelli reaction under solvent free conditions

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Nano-ZrO_2 sulfuric acid [n-ZrO_2-SO_3H (n-ZrSA)] has been synthesized from the reaction of nano-ZrO_2 with chlorosulfonic acid as sulfonating agent. This catalyst was characterized *via* FT-IR, XRD, TGA, FESEM, TEM, EDX, BET, BJH, ICP and pH analysis. We show that n-ZrSA catalyzed Biginelli reaction for the synthesis of 3,4-dihydropyrimidin-2(1*H*) one derivatives in high yields under solvent-free conditions by the reaction of aldehyde, *β*-diketoester and urea (or thiourea). Main advantages of the catalyst are its non-toxic nature, high stability and reusability.

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1. Introduction

Introduction of acid catalysts is one of the most frequently applied processes in chemical industry, which has been a major area of research interest.[1-5] The need for development of heterogeneous catalysts has arisen from the fact that homogeneous catalysts pose several drawbacks. These flaws include equipment corrosion, production waste, difficulty separation and recycling, high cost and low efficiency. In this regard, heterogeneous catalysts compensates the disadvantages mentioned of homogeneous catalysts, because they have the benefit of decreasing corrosion, non-toxic, ease of handling, high selectivity, easy separation and reusability to render the process as green.[6-11]

The commonly used support for the more facile heterogeneous catalytic synthesis are polymers, mesoporous materials,[12] metal oxides[13] and nanoparticles.[14] In the last decade, the synthesis and application of metal oxide nanoparticles as heterogeneous catalysts with different shapes and sizes have been developed. Solid acid nano catalysts that are bridge between homogeneous and heterogeneous catalysts, exhibit higher activity and selectivity than their corresponding bulk materials. They are expected to be suitable candidates for the design of highly active and selective heterogeneous catalysts for organic synthesis due to their unique physical, surface chemical and catalytic properties and large surface-to-volume ratio. In addition, transport pathways of reactants and products in the nanomaterial-based catalysts could be significantly shortened unlike many heterogeneous support matrices where a great portion of catalyst sites are present deep inside the matrix backbones and reactants have only limited access to the catalytic sites.[15, 16]

Sulfonation with chlorosulfonic acid[17, 18] is an efficient procedure for heterogenization of homogeneous catalysts that has been much attention after Zolfigol's report on the preparation of silica sulfuric acid.[19]

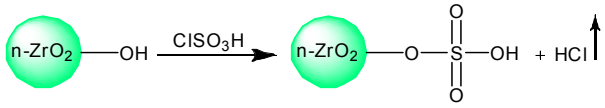
Zirconia (ZrO_2) is one of the most important ceramic materials that are widely used in chemical industry due to their unique electrical, mechanical, optical and thermal properties.[20-22] In this regard, significant progress in the synthesis of nano-Zirconia has been made over the last decades and most applications of these novel materials have been directed toward acid-catalyzed reactions. In addition zirconia has attracted considerable interest on account of its potential application as a catalyst support.[23-26]

Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (DHPMs) have attracted great attention recently in synthetic organic chemistry due to their pharmacological and therapeutic properties.[27-30] The reaction is accomplished from one-pot condensation of *β*-dicarbonyl compound, aldehyde and urea or (thiourea) in the presence of various catalyst. A wide range of sulfunated solid acid catalysts such as silica sulphuric acid,[31] cellulose sulfuric acid,[32] alumina sulfuric acid,[33] tungstate sulfuric acid,[34] molybdate sulfuric acid[35] and perlite sulfonic acid[36] have recently been used for this reaction.

Based on the above fundamental understandings and in continuing our efforts towards the development of efficient and environmentally benign heterogeneous catalysts, [36-38] we prepared a green solid acid nano-catalyst ZrO_2–SO_3H (n-ZrSA) that has been applied for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.

2. Results and Discussion

Due to the considerations needs to clean and green recovery of the heterogeneous solid acid catalyst, we prepared nano-ZrO_2 sulfuric acid (n-ZrSA) as a new heterogeneous solid acid nano catalyst. Firstly, nano zirconia was prepared. Then, the reaction of n-ZrSA with chlorosulfonic acid in dry CH_2Cl_2 at 0 ˚C gave Nano-ZrO_2 sulfuric acid (n-ZrSA) (Scheme 1). The synthesized catalyst was characterized by different methods such as IR, FESEM, TEM, XRD, TGA, EDX, BET, BJH, ICP and acid–base titration.



Scheme 1. Preparation of nano-ZrO_2-SO_3H (n-ZrSA)

2.1. Catalyst characterization

2.1.1. FT-IR spectra

Fig. 1 shows the FT-IR results of the synthesized nano-ZrO_2 powder with and without SO_3H loading, respectively. It revealed the presence of major bands at 757 and 584 cm^{-1} which are attributed to the strong stretching vibrations of the Zr–O group. The vibration bands at around 1649 cm^{-1} is due to Zr–OH vibration and the absorbance band at around 3434 cm^{-1} was certified to the adsorbed water (Fig. 1, graph a and b) which is consistent with the reported IR spectra for nano-ZrO_2.[39] In the sulfuric acid-functionalized nano-ZrO_2 (Fig. 1b), some new bands appeared at 825–881 and 1059–1172 cm^{-1}, which are attributed to the O=S=O asymmetric and symmetric stretching vibration and S-O stretching vibration of the sulfonic groups (-SO_3H), respectively. The spectrum also shows a relatively broad band around 2700–3600 cm^{-1} due to OH stretching absorption of the SO_3H group. All these observations confirm that the sulfonic groups have functionalized the surface of the nano-ZrO_2.

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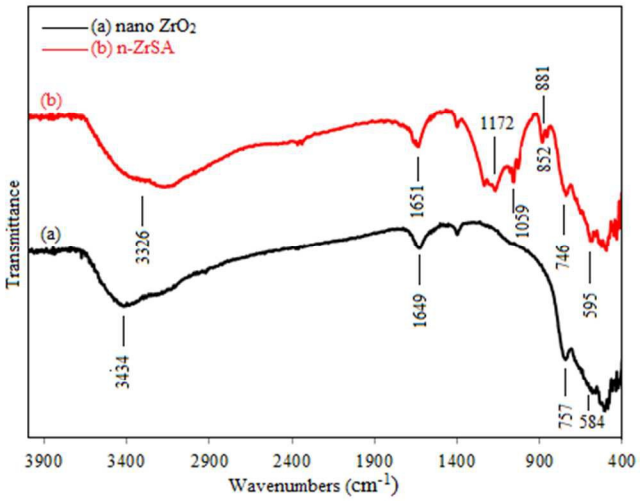

Fig. 1. FT-IR spectra of (a) nano ZrO_2 (b) n-ZrSA

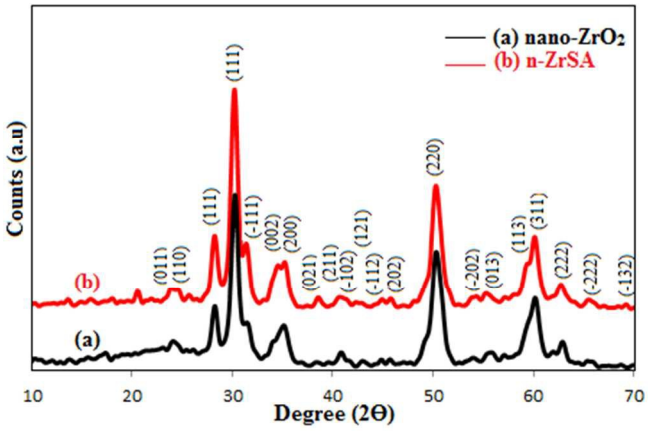

Fig. 2. Powder XRD patterns of (a) nano ZrO_2 (b) n-ZrSA

2.1.2. X-ray diffraction (XRD) analysis

Fig.2a is the X-ray powder diffraction pattern for the ZrO_2 nanoparticles before modification. Combination of both phases' tetragonal ZrO_2 and monoclinic ZrO_2 morphologies are clearly shown according to the XRD. As can be seen, the broad diffraction peaks are assigned to (111), (002), (200), (220), (113), (311) and (222) reflections of tetragonal ZrO_2 which coincides with JCPDS card no 14-0534. The following peak signals with miler indices (011), (110), (111), (-111), (002),(200), (021), (211), (-102), (121), (-112), (202), (220), (-202), (013), (113), (311), (222), (-222) and (-132) in Fig. 2a confirm the formation of monoclinic ZrO_2, which coincides well with the standard data for monoclinic ZrO_2 (JCPDS No. 07-0343).

The crystal size of the nano ZrO_2 powder was also determined from X-ray pattern using the Debye-Scherrer formula given as $t=0.9\lambda/B1/2\cos\theta$, that t is the average crystal size, λ the X-ray wavelength used (1.54 Å), $B_{1/2}$ the angular line width at half maximum intensity and θ the Bragg's angle. The average crystal size of the nano-ZrO_2 powder for $2\theta= 52.18^{o}$ is calculated to be around 10 nm. Fig.2b illustrates XRD patterns of the samples of modified nano-ZrO_2. As shown in Fig.2b, the peak intensities of n-ZrSA are almost the same as those of nano-ZrO_2 (Fig. 2a) and sulfonate modification does not change the phase of nano-ZrO_2.

2.1.3. Thermo gravimetric analysis (TGA)

The thermal behaviour of n-ZrSA and pure nano-ZrO_2 is shown in Fig. 3. The results indicate that nano-ZrO_2 (Fig. 3a) showed a weight loss (3 wt.%) below 120 ˚C which corresponds to the loss of the physically adsorbed water and then had a steady weight loss (3 wt.%) at the temperature lower than 800 ˚C, which possibly corresponds to the dehydroxylation of ZrO_2. The TGA analysis of n-ZrSA (Fig. 3b) shows two-stages decomposition, completely different from nano-ZrO_2. A significant decrease in the weight percentage (4 wt.%) of the n-ZrSA at about 154 ˚C to is due to the slow decomposition of covalently bounded SO_3H groups. Finally, a mass loss of approximately 8% weight occurred between 590 and 660 ˚C that is related to the sudden mass loss of SO_3H groups.[40-42] Also, from the TGA, it can be understood that ZrSA has a great thermal stability (up 150 ˚C) confirming that it could be safely used in organic reactions at temperatures in the range of 80-140 ˚C.

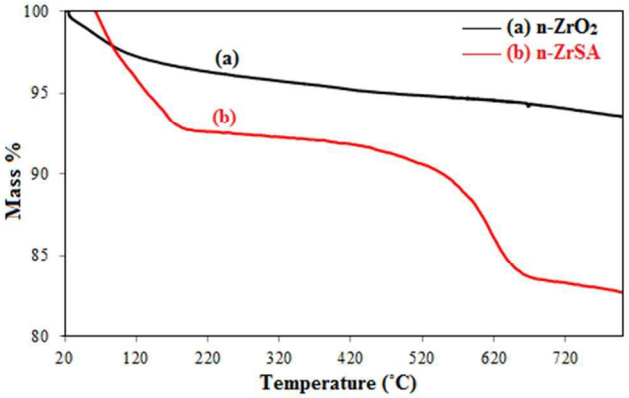

Fig. 3. TGA spectra of (a) nano ZrO_2 (b) n-ZrSA

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2.1.4. FE-SEM and TEM analysis

Field emission scanning electron microscopy (FESEM) images of the obtained materials were recorded to show the surface morphological changes occurred on the catalyst due to the modification of nano-ZrO_2. It is evident that the morphology size and distribution of the nanoparticles are almost homogeneous; and the particle size has increased after the modification (Fig. S1, ESI†). The TEM images as well as the particle size distribution profile are shown in Fig. 4a-e, respectively. As could be seen from Fig. 4, the material is mainly consisted of spherical particles. According to the Fig. 4c the particle diameter size is 20 nm. It also indicates that the maximum particle size distribution was in the range of 20-30 nm.

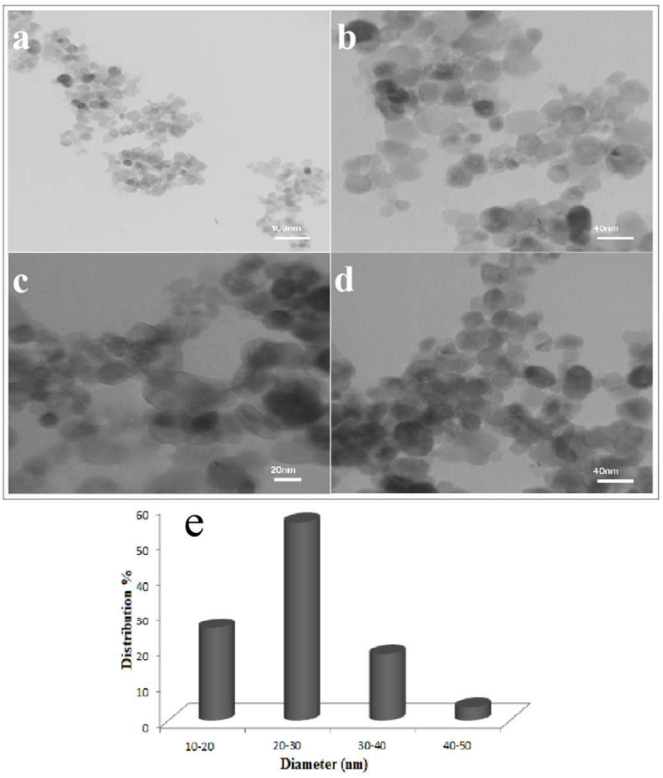

Fig. 4. TEM images of the synthesized n-ZrSA nanomaterial and particle size distribution

2.1.5. EDX analysis

Energy-dispersive X-ray spectroscopy (EDX) analysis of n-ZrSA indicated the presence of Zr, O, S as the components of n-ZrSA structure that confirm the formation of SO_3H groups after modification of n-ZrO_2 by sulfunation agent (Fig. S2, ESI†).

2.1.6. BET and BJH texture analysis

The surface area and pore volume and pore size of the catalyst were calculated using the Brunauer-Emmett-Teller (BET) and BJH equations. BET surface area was acquired on a Beckman Coulter SA3100 Surface Area Analyzer. Prior to N_2-physical adsorption measurements, catalyst was degassed at 150 ˚C for 120 min in the nitrogen atmosphere. The specific surface area (SBET) of the n-ZrSA was determined with adsorption-desorption isotherms of N_2 at 77 K. The surface area, pore volumes and pore width of the catalyst are summarized in table 1. Also, Table 2 shows the textural properties of n-ZrSA.

Table 1. BET data showing the textural properties of n-ZrSA

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore width (nm)
n-ZrSA	15.5	0.0125	1.7

Table 2. BJH data showing the textural properties of n-ZrSA

Sample	n-ZrSA
Desorption Pore Diameter	8.6 nm
Cumulative Desorption Pore Volume	0.062 cm^3/g
Desorption Surface Area	21.6 m^2/g

2.1.7. PH analysis of catalyst

The optimum concentration of H^+ of ZrSA was determined by acid-base potentiometric titration of the aqueous suspension of the weighed amount of thoroughly washed catalyst with standard NaOH solution. At first 100 mg ZrSA was dispersed in 20 ml H_2O by ultrasonic bath for 60 min at room temperature after which the pH of solution was 1.62. The amount of the acid was neutralized by addition of standard NaOH solution (0.085 N) to the equivalence point of titration. The required volume of NaOH to this point was 3.41 ml. This is equal to a loading of 2.9 mmol H^+/g.

2.2. Catalytic performances in multicomponent one-pot synthesis of dihydropyrimidinones

After characterization, catalytic activity of the catalyst was examined in the synthesis of dihydropyrimidinone derivatives. In a model reaction and in the reaction between ethyl acetoacetate, urea and benzaldehyde, the effect of the catalyst amount was investigated (Table 3). To minimize the formation of byproducts and to achieve good yield of the desired product, the reaction is optimized by varying the amount of catalyst (5, 10, 15 and 20 mol%). The percentage of the product formation using n-ZrSA as the catalyst was found 86, 98, 90 and 83%, respectively (Table 3, entries 2-5). Therefore, it was found that the use of 10 mol% of the catalyst was sufficient to promote the reaction. Larger amounts of the nanocatalyst were found to have an inhibitory effect on the formation of the product (entries 4 and 5). The catalytic activity of n-ZrSA was evident when trace product was obtained in the absence of the catalyst (entry 1). The same reaction in the presence of 10 mol% of n-ZrSA was carried out at different temperatures (60, 90, 100, 120 ˚C) under solvent-free conditions to assess the effect of temperature on the reaction yield.

The yield increased as the reaction temperature was raised. At 90 ˚C, product was obtained in high yield within 30 min. A further increase in temperature and time did not improve the product yield (entries 7 and 8). To investigate the effect of the solvent on the catalytic reaction, the model reaction in the presence of 10 mol% of n-ZrSA was carried out in various solvents under reflux conditions (Table 3, entries 9-11). The result shows that the MeOH is the best solvent in terms of the time and yield (Table 3, entry 11). There are also more efficient, as well as solvent-free conditions. Because of the toxicity of organic solvents, we considered green media. When the reactions were conducted in solvent-free conditions, the expected products

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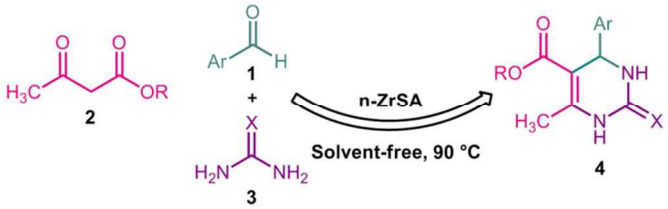
were obtained with excellent yields in low reaction times (Table 3, entry 3).

According to the optimization results, several substituted aromatic aldehydes were reacted with ethyl acetoacetate (or methyl acetoacetate) and urea (or thiourea) in the presence of 10 mol% n-ZrSA at 90 ˚C under solvent-free condition (Scheme 2). In all cases, the three-component reaction proceeded smoothly to give the corresponding 3,4-dihydropyrimidin-2(1*H*)-ones/thiones in moderate to good yields. The reaction with aromatic aldehydes carrying electron-donating or electronwithdrawing groups gave the corresponding product in good yields and high purity. Thiourea also provided the Biginelli products in moderate yields (Table 4, entries 1–21).



Scheme 2. Synthesis of DHPMs catalyzed by n-ZrSA

Table 3. Optimization of synthesis of dihydropyrimidinones[a]

Entry	Solvent	Condition	Amount of Catalyst (mol%)	Time (min)	Yield (%)
1	Solvent-free	90 ˚C	-	50	Trace
2	Solvent-free	90 ˚C	5	50	86
3	Solvent-free	90 ˚C	10	30	98
4	Solvent-free	90 ˚C	15	50	78
5	Solvent-free	90 ˚C	20	50	83
6	Solvent-free	60 ˚C	10	50	83
7	Solvent-free	110 ˚C	10	50	85
8	Solvent-free	120 ˚C	10	50	89
9	EtOH	Reflux	10	50	45
10	MeOH	Reflux	10	50	91
11	H_2O	Reflux	10	50	Trace

[a] Benzaldehyde 1 (1 mmol), ethylacetoacetate 2 (1 mmol), urea 3 (1.2 mmol).
[b] Refers to isolated yield.

Table 4. n-ZrSA-catalyzed one-pot synthesis of dihydropyrimidinones[a]

Entry	Ar	R	X	Product	Time (min)	Yield[b] (%)	mp (˚C)	
							Found	Reported
1	Ph	Et	O	4a	30	98	202-204	202-204[43]
2	4-HOC_6H_4	Et	O	4b	20	97	233-235	231-233[44]
3	2-ClC_6H_4	Et	O	4c	70	96	222-224	222-224[43]
4	4-ClC_6H_4	Et	O	4d	70	91	214-216	214-216[43]
5	3-HOC_6H_4	Et	O	4e	55	70	169-171	167-170[45]
6	2-HOC_6H_4	Et	O	4f	40	76	201-203	201[45]
7	2-$MeOC_6H_4$	Et	O	4g	50	93	262-264	260[44]
8	4-$MeOC_6H_4$	Et	O	4h	35	97	204-206	202-204[44]
9	3,4-$MeOC_6H_3$	Et	O	4i	55	75	177-179	178[43]
10	3-EtO-4-HOC_6H_3	Et	O	4j	55	98	194-196	193-195[43]
11	4-MeC_6H_4	Et	O	4k	60	86	215-217	216-218[43]
12	3-$O_2NC_6H_4$	Et	O	4l	80	72	225-227	227-228[44]
13	4-$O_2NC_6H_4$	Et	O	4m	45	92	208-211	208-210[46]
14	4-MeC_6H_4	Me	O	4n	50	97	210-212	210-213[44]
15	3-EtO-4-HOC_6H_3	Me	O	4o	40	96	253-254	253-254[47]
16	4-ClC_6H_4	Me	O	4p	40	99	204-206	203-205[44]
17	4-$(CH_3)_2NC_6H_4$	Me	O	4q	40	95	213-215	213-215[47]
18	C_6H_5	Me	S	4r	40	94	225-226	221-222[44]
19	C_6H_5	Et	S	4s	40	98	212-214	212-214[44]
20	4-HOC_6H_4	Et	S	4t	42	90	204-206	202-203[48]
21	4-$O_2NC_6H_4$	Et	S	4u	45	91	193-195	193-194[49]

[a] All products were characterized by IR, ^{1}H NMR spectroscopic data, and melting points.
[b] Yields refer to isolated products.

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Table 5. Comparison study of the efficiency of the n-ZrSA with some different reported catalysts in Biginelli reaction

Entry	Catalyst	Condition	Time (h)	Yield (%)	Ref.
1	MCM-41-R-SO_3H[a]	MeCN /Reflux	3	94	[50]
2	12-Tungstophosphoric acid	AcOH /Reflux	6	98	[51]
3	$HClO_4$-SiO_2	Solvent-free/100 ˚C	1.5	90	[52]
4	Bentonite/PS-SO_3H	Solvent-free/120 ˚C	0.5	89	[53]
5	CSA[b]	H_2O/100 ˚C	5	80	[54]
6	DBSA[c]	Solvent-free/80 ˚C	3	94	[55]
7	Nafion NR-50	MeCN /Reflux	3.5	95	[56]
8	TCCA[d]	EtOH/Reflux	12	94	[57]
9	n-ZrSA	Solvent-free/90 ˚C	0.5	98	Peresent work

[a] MCM-41 anchored sulfuric acid
[b] Cellulose sulfuric acid
[c] *p*-dodecylbenzenesulfuric acid
[d] trichloroisocyanuric acid

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To show the merit of the present work in comparison with reported results in the literature, we compared the results of n-ZrSA catalyst with reported catalysts in the Biginelli reaction (Table 5).

2.3. Plausible mechanism

A plausible mechanism for the Biginelli reaction in the presence of n-ZrSA is depicted in (Fig. S3, ESI†). Probably, this transformation is triggered by an initial activation of aldehyde **1** by protonation which then undergoes Knoevenagel condensation with β-ketoester **2** forming intermediate **I** and after dehydration gives the olefin **II**. Nucleophilic attack of the amino group in urea or thiourea **3** at the *β*-carbon of the *α,β*-unsaturated carbonyl group followed by cyclization yields the product **4**.

2.4. Reusability of the catalyst

One of the most important advantages of heterogeneous catalysis is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst was investigated in the Biginelli reaction. After completion of the reaction, the catalyst was separated by centrifuging, washed with hot ethanol and acetone and dried in oven. Then the recovered catalyst was used in the next run. The results of five consecutive runs showed that the catalyst can be reused 5 times without significant loss of its activity (Fig. 5). ICP analysis of fresh and recycled catalyst showed 3.8% and 2.7% of S content respectively.

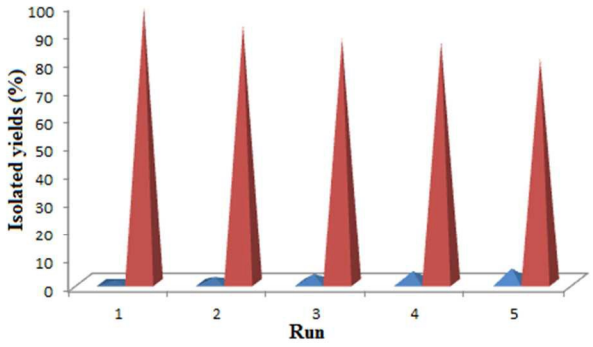

Fig. 5. Reusability of n-ZrSA in Biginelli reaction

3. Experimental section

3.1. General Remarks

All chemicals reagents were purchased from Merck and Fluka and used without any further purification. Solvents were purified by conventional methods. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Shimadzu 8400s spectrometer using KBr pressed powder discs. The crystal structure of synthesized materials was obtained with a Siemens D5000 (Siemens AG, Munich,Germany) X-ray diffractometer using Cu-Ka radiation of wave-length 1.54˚A. Thermal analysis was done by using a thermogravimetric analyzer on a Du Pont 2000 thermal analysis apparatus at a heating rateof 5 ˚C min^{-1} under air atmosphere. Field emission scanning electron microscope (FESEM) images were acquired with a Philips XL30 field emission scanning electron microscope (Royal Philips Electronics, Amsterdam, The Netherlands instrument operating at 10 kV. ZrO_2 nanoparticles were dispersed in water and cast onto a copper grid to study the sizes and morphology of the particles by TEM (Transmission Electron Microscopy) using a Philips – CM300 - 150 KV microscope. The average particle size distribution was carried out using Image software. The EDX characterization of the catalyst was performed using a Mira 3-XMU scanning electron microscope equipped with an energy dispersive X-ray spectrometer operating. BET surface area was acquired on a Beckman Coulter SA3100 surface area analyzer.
The loading value of sulfur in the catalyst was estimated by inductively coupled plasma ICP analysis with a ICP MS ELAN DRC-e. The NMR spectra were recorded with a Bruker Avance 300 MHz instruments (^{1}H NMR 300 MHz) in pure deuteriated chloroform and dimethyl sulfoxide with tetramethylsilane (TMS) as the internal standard. The purity of products was checked by thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using n-hexane/ethyl acetate mixture as mobile phase.

3.2. Preparation of nano-ZrO_2

Initially, a solution of $ZrOCl_2.8H_2O$ (0.5 M) in $EtOH/H_2O$ (40:10) was prepared. Conc. $NH_3{\cdot}H_2O$ was diluted to a solution (the concentration of it was twice that of the $ZrOCl_2$ solution) with the same solvent and was then added dropwise at rate of 3 ml/min to the vigorously stirred $ZrOCl_2$ solution. A white, gelatinous hydroxide precipitate was filtrated, washed with $EtOH/H_2O$ in order to remove starting materials, dried at 100 ˚C for 2h and calcined at 600 ˚C for 2h, ZrO_2 nanoparticles with white colour were obtained.[58]

3.3. Preparation of nano-ZrO_2-SO_3H (n-ZrSA)

ZrO_2 nanoparticles (1g) in dry CH_2Cl_2 (20 ml) was added to a suction flask that was equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water). Then chlorosulfonic acid (0.25 ml, 3.76 mmol) was added dropwise over a period of 20 min in an ice bath (0 ˚C). After completion of the addition, the reaction mixture is allowed to stand for 1 h at room temperature, while the residual HCl was eliminated by suction vessel. Solid powder was washed with water (10 mL) and dried at 80 ˚C. Nano-ZrSA (1.15g) was obtained as a solid acid catalyst in the organic synthesis.

3.4 General procedure for the synthesis of 3,4-dihydopyrimidin-2(1*H*)-ones

In a typical procedure, a mixture of aromatic aldehyde (1 mmol), *β*-dicarbonyl compounds (1 mmol), urea (or thiourea) (1.2 mmol) was stirred at 90 ˚C utilizing *n*-ZrSA (0.034g, 10 mol%) in

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solvent free condition for the appropriate time until the reaction was complete. Completion of the reaction was monitored by Thin Layer Chromatography (TLC) [7:3 n-hexane:ethyl acetate]. After the completion of the reaction, the reaction mixture was cooled, eluted with hot ethanol (5 mL), centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure 3,4-dihydopyrimidin-2(1*H*)-ones derivatives.

3.5. General procedure for recycling of n-ZrSA

Recyclability of the catalyst was tested for the synthesis of 3,4-dihydopyrimidin-2(1*H*)-ones between benzaldehyde (1 mmol), ethylacetoacetate (1 mmol) and urea (1.2 mmol) under solvent-free condition at 90 ˚C. After completion of the reaction, the heterogeneous catalyst was separated from the production mixture by centrifuging, washed with hot ethanol (2*15 ml), hot acetone (2*10 ml) to remove the organic compounds and dried in oven to be used in the next cycles. In every run, the yield of product was performed in constant time. This process was repeated 5 more times, affording the desired product in good yields, with undiminishing efficiency.

4. Conclusion

In summary, for the first time nano-ZrO_2 sulfuric acid (n-ZrSA) was introduced as a heterogeneous highly powerful solid acid catalyst for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones under solvent-free conditions. All the reactions work easily for a variety of aldehydes with both electron-donating and electron-withdrawing groups to give corresponding products in excellent yields.

The catalyst was reused for 5 consecutive cycles with consistent activity. The excellent catalytic performance, easy preparation and separation of the catalyst make it to be a good heterogeneous solid acid nano catalyst for organic synthesis and transformations. In addition, good yields, low-cost, short reaction times, non-toxicity, solvent-free conditions and a recyclable catalyst is supporting methods toward the green chemistry.

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Notes

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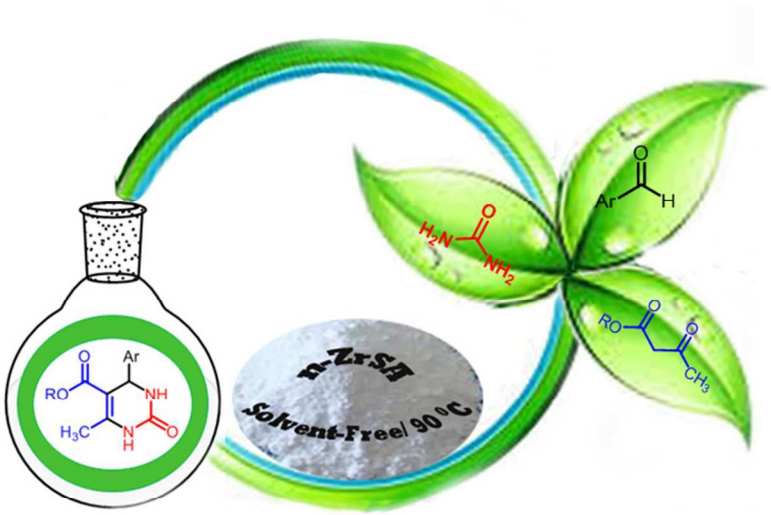

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