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TS-1 zeolite as a Lewis acid catalyst for solvent-free one-pot synthesis of 1,3-thiazolidin-4-ones

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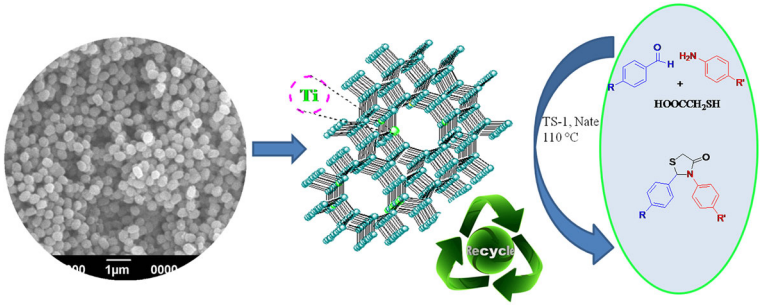
Abstract

Titanium silicate (TS-1) zeolite heterogeneous catalyst is synthesized by the hydrothermally discontinuous method and is characterized by using XRD, SEM, TEM, and NH_3–TPD techniques. The catalytic activity of the TS-1 type zeolite was tested for one-pot solvent-free synthesis of 1,3-thiazolidine-4-ones. The present technique illustrates many benefits, including eco-friendly reaction conditions, environmentally helpful, short response time, simplicity, straightforward separation, catalyst reusability and high yields of the products. Furthermore, the catalyst was utilized for four recycle reactions and it has been found that the catalyst shows consistent chemical process activity.

Graphical abstract



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Keywords Lewis acid · Titanium silicate (TS-1) · 1,3-Thiazolidin-4-ones · Zeolite catalyst · Synthesis

Introduction

In last 2–3 decades, researchers have had much more interest in the synthesis of heterocyclic (mainly O, N, S, containing) compounds, because of increasing demand of pharmaceutical products, agrochemicals, veterinary products and use of everyday life. Also, they are used in sanitizers, antioxidants, as corrosion inhibitors, as co-polymers, and dyestuff. They are used as catalysts, as well as vehicles in the synthesis of other organic transformation. Some heterocyclic compounds found in natural products, antibiotics (penicillins), alkaloids (morphine), etc. have many applications in heterocyclic moiety [1, 2]. Here, we have synthesized 1,3-thiazolidin-4-ones heterocyclic compounds, which has much more importance in medicinal chemistry (Fig. 1).

4-Thiazolidinone derivatives are a promising class of heterocycles, which represent a class of chemical products with interesting pharmacological and biological activities such as antidiabetic activity, anticonvulsant, DNA cleavage [3, 4], anti-histaminic [5], antifungal [6], antihypersensetive [7], anti-infective [8], antitubercular [9], antiviral [10], anti-cancer, antituberculotic [11, 12], antimicrobial [13], antioxidant [14], analgesic [15], antiviral, anti-HIV [16, 17], in ibuprofen anti-inflammatory drugs [18, 19], antimicrobial [20, 21]; toxicological 4-thiazolidinone derivatives are genotoxically safe [22].

In a recent trend, one-pot synthesis methodology has taken on a major role in organic transformation attributable to its many benefits including atom economy, high yield property, minimum latency and least by-products as compared to classical artificial methods [23]. Nitrogen, sulfur-containing heterocyclics are the building blocks of natural products and drug molecules; nearly 60% of unique small molecule drugs contain a nitrogen heterocycle [24, 25]. Considering these wide and versatile applications, few catalytic methods have been developed for the synthesis of biologically active 1,3-thiazolidin-4-ones derivatives, such as DIPEA in the presence of toluene 24–36 h, $SnCl_2$ and acetic acid 14 h [18, 19, 26], nano Cd-Zr_4-$[PO4]_6$, [24, 25], *N*-methyl pyridinium tosylate [27], ammonium persulfate [28], ionic liquid [bmim] OH [29], $Bi[SCH_2COOH]_3$ [30] acid catalysed [31] silica supported Co-Fe_2O_4@SiO_2/$PrNH_2$ [32], $Y[OTf]_3$ [33]. Although reported methods are quite efficient, some suffer from one or more types of limitations such as more reaction time, harsh reaction conditions, carcinogenic or hazardous materials, volatile organic/other solvents, homogeneous catalyst separation, low yield and use of an expensive catalyst. Some of the reported catalysts are not reusable and some methods require special conditions, such as microwave or sonication, require high temperature, homogeneous-phase reactions, etc. [29, 34]. Hence, to overcome these limitations, it is necessary to find sustainable, efficient, eco-friendly and cost effective protocols for synthesis of 1,3-thiazolidin-4-ones derivatives. So, we have developed a TS-1 catalyst and firstly reported here a sustainable, eco-friendly, cost

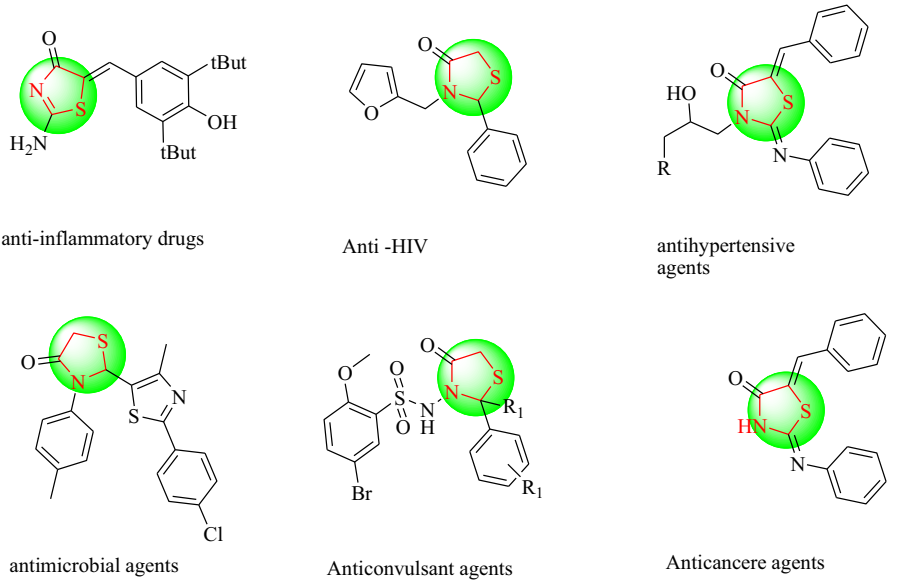


Fig. 1 Biologically important thiazolidin-4-ones derivatives

effective, efficient protocol for synthesis of 1,3-thiazolidin-4-ones derivatives. It has a heterogeneous solid acid catalyst, as well as strong Lewis and Bronsted acidic properties [35–37]. Titanium silicate [TS-1] zeolite is an alternative active heterogeneous Lewis acid catalyst possessing unique properties such as high surface area, high thermal stability, non-toxicity, reusability, and ease of handling, hence is utilized in various industrial processes such as oxidation, epoxidation, alkylation, acylation and cyclic condensation reactions [38–40]. In view of the ever increasing importance of green/sustainable synthetic protocol, it was aimed to develop eco-friendly, efficient catalytic methods for organic synthesis.

Experimental

Preparation TS-1

A Lewis acid catalyst, titanium silicate (TS-1), was prepared by using the reported method [41]. Titanium tetrabutoxide ($Ti[OBu)_4$] 1.16 mL was mixed in 30 mL of solvent (dry alcohol) and stirred vigorously, Tetraethyl ortho-silicate (TEOS) 24.37 mL and 20% tetrapropyl ammonium hydroxide (TPA-OH) 25 mL was added with vigorous stirring, resulting mixture was stirred for 10 min at 30–35 °C to obtain silica sol. The prepared titanium containing gel was added into the silica sol with constant stirring at 70–75 °C for 60–120 min to remove excess solvent. The final transparent gel maintained basic pH, and was transferred to the autoclave, autogenously pressure at 175 °C for 24 h discontinuously, then treated hydrothermally under static condition. The solid product was filtered, dried at 100 °C for 1 h,

and calcined at 500 °C for 4 h under air atmosphere. The subsequent material was normally cooled, portrayed and called Lewis acid catalyst titanium silicate (TS-1).

General procedure for one-pot synthesis of 1,3-thiazolidin-4-ones

A mixture of substituted 4-chloro benzaldehydes (0.140 g, 1 mmol), thioglycolic acid (0.092 g, 1 mmol) and 4-chloro anilines (0.127 g, 1 mmol), 0.05 g of TS-1 catalyst, was magnetically stirred, then gradually the temperature was increased, and refluxed at 110 °C. The progress of the reaction was monitored by TLC using ethyl acetate/ether as a solvent system. The reaction mixture was quenched with crushed ice and extracted with ethyl acetate (3 × 25 mL). Simultaneously, the catalyst was recovered for next batch reaction. The organic extracts were washed with brine (3 × 25 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to afford the corresponding crude compounds. The obtained crude compounds were recrystallized using ethanol to afford pure products (**3a**–**i**).

Results and discussion

In continuation, the synthesised catalyst was characterised by powder X-ray diffraction patterns of TS-1 calcined at 500 °C, as is shown in Figs. 2 and 3, and show intense peaks at $2\theta^\circ$ = 14.63, 21.81, 22.76, 22.59, 24.04, and 26.62 with corresponding planes (112), (023), (150), (511), (250), (004). The planes (150) and (511) indicate the presence of ordered orthorhombic, MFI topology TS-1 framework [42, 43]. The SEM and TEM images suggest that the prepared catalyst has uniform spherical particle size and hexagonal shape with ordered morphology; similarly, they show high acidity, calculated by NH_3–TPD analysis, shown in Table 1. For the synthesised catalyst TS-1, the total acidity (Lewis and Bronsted) is calculated by using the following formula.

$$\text{Acidity} = \frac{\text{Volume of } NH_3 \text{ Desorbed}}{22.4256} \text{ m mol/gm}$$

Optimization of reaction conditions

In order to find the optimum loading of the catalyst in the reaction of 4-chloro benzaldehydes (1 mmol), thioglycolic acid (1 mmol), 4-chloro anilines (1 mmol), and TS-1 catalyst, initially, many protic and aprotic solvents and acceptable times were screened with loading calcined TS-1 catalyst reflux condition, and the results are summarized in Table 2. A model reaction (**3b**) has completely different quantity of calcined TS-1 catalyst screened with reflux condition and the results are summarized in Table 3. In the absence of a catalyst the reaction didn't give satisfactory results of the specified product (**3b**) within the stipulated time. However, reaction yields were found more in solvent-free conditions as compared to other solvents. It has been found that refluxing the reaction mixture at 110 °C for

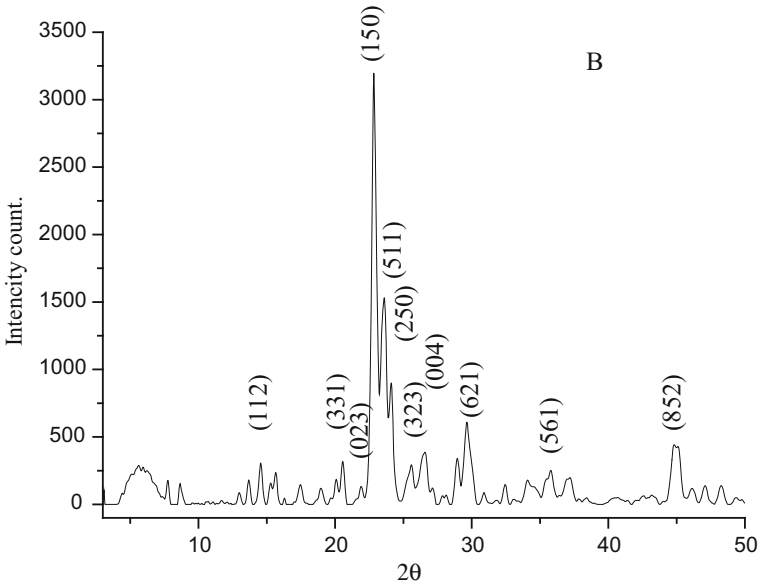


Fig. 2 Powder XRD pattern of TS-1 calcined at 500 °C

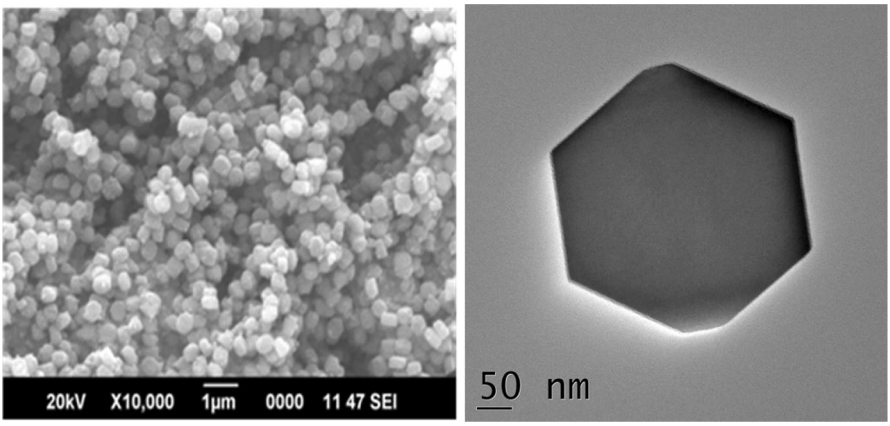


Fig. 3 SEM and TEM patterns of TS-1 calcined at 500 °C

Table 1 Total acidity of TS-1 catalyst

Peak no.	Temperature (°C)	Volume (mL/g STP)	Peak height	Acidity (mmol/g)	Total acidity (mmol/g)
1	238.5	2.99301	0.08150	0.1334	0.4856
2	423.3	7.89957	0.04531	0.3522	

Table 2 Effect of various solvents in the synthesis of **3b**

Entry	Solvent	Yield (%)[a]
1	Water	Trace
3	Ethanol	35
4	PEG	40
5	THF	50
6	Chloroform	60
7	Solvent-free	90

[a]Isolated yield

Table 3 Effect of the amount of TS-1 on modal reaction **3b**

Catalyst (mg)	Time (min)	*T* (°C)	Yield (%)[a]
–	500	rt	–
–	60	110	Trace
10	30	110	20
30	30	110	50
50	30	110	90
70	30	110	90
50	60	120	90

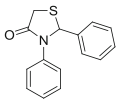
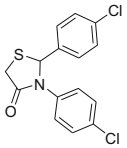
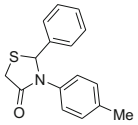
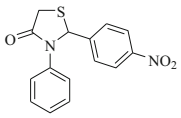
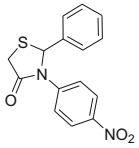
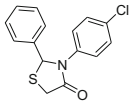
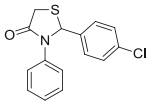
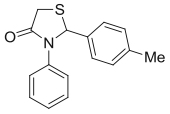
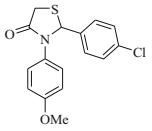
[a]Isolated yield

10–30 min with loading 0.05 g of TS-1 is an appropriate reaction condition for the synthesis of 1,3-thiazolidin-4-ones derivatives.

In order to explore the scope and importance of the present method, under optimized conditions, electronically diverse TS-1 catalyst was tested for the synthesis 1,3-thiazolidin-4-ones derivatives, and the results are summarized in Table 4. It was found that substituted aryl aldehyde and substituted aniline with electron donating and withdrawing groups. It was found that the electron withdrawing groups give maximum yield as compared to the electron donating groups. After optimizing reaction conditions, efforts have been made towards the recovery and reusability of the catalyst (Scheme 1).

The plausible reaction mechanism for the formation of 1,3-thiazolidin-4-ones has been depicted in Fig. 4. (I) A more reactive lone pair of RCHO interacts with Lewis acid catalyst to enhance electrophilicity and nucleophile RNH_2 interacts immediately. Simultaneously, the catalyst acts as a Bronsted base and accelerates the reaction to form a carbon–nitrogen bond (C=N) (III). Respectively, the catalyst again acts as a Lewis acid to interact (III) and enhance electrophilicity (C=N). The thioglycolic acid –SH group acts as nucleophile. Simultaneously, the catalyst acts as a Bronsted base to accelerate reaction forward (IV) of intermediates, then rearranges and cyclization and dehydration give compounds (V), target molecule 1,3-thiazolidin-4-ones (**3a**–**i**).

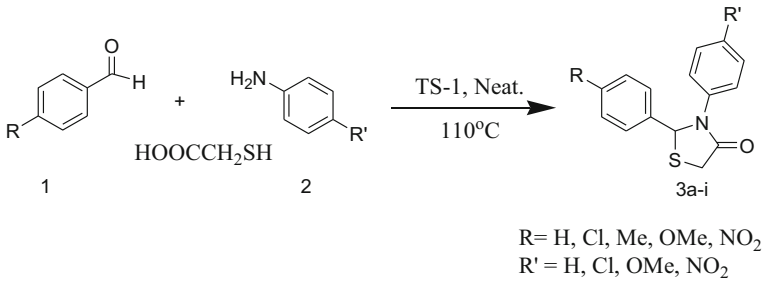
Table 4 TS-1 catalyzed synthesis of 1,3-thiazolidin-4-ones derivatives

Entry	Mol. formula product	*R*	R_1	Yield (%)[b]	M. P. Obs. (°C)	M. P. Lit. (°C)
3a		H	H	89	128–130	129–131 [44]
3b[a]		Cl	Cl	90	167–1688	168 [46]
3c		H	CH_3	85	106–107	105–107 [44]
3d		NO_2	H	90	127–130	105–106 [30]
3e		H	NO_2	90	129–131	133–134 [45]
3f		H	Cl	88	122–123	121–123 [30]
3g		Cl	H	86	123–124	123–124 [30]
3h		CH_3	H	85	116–118	116–118 [44]
3i		Cl	OCH_3	88	154–155	154 [46]

Reaction conditions: substituted aryl benzaldehyde 1,4-chloro aniline 2, and thioglycolic acid 3, and TS-1 (0.05 g) solvent-free

[a]Model reaction **3b**

[b]Isolated yields



Scheme 1 The synthetic pathway of compounds **3a–i**

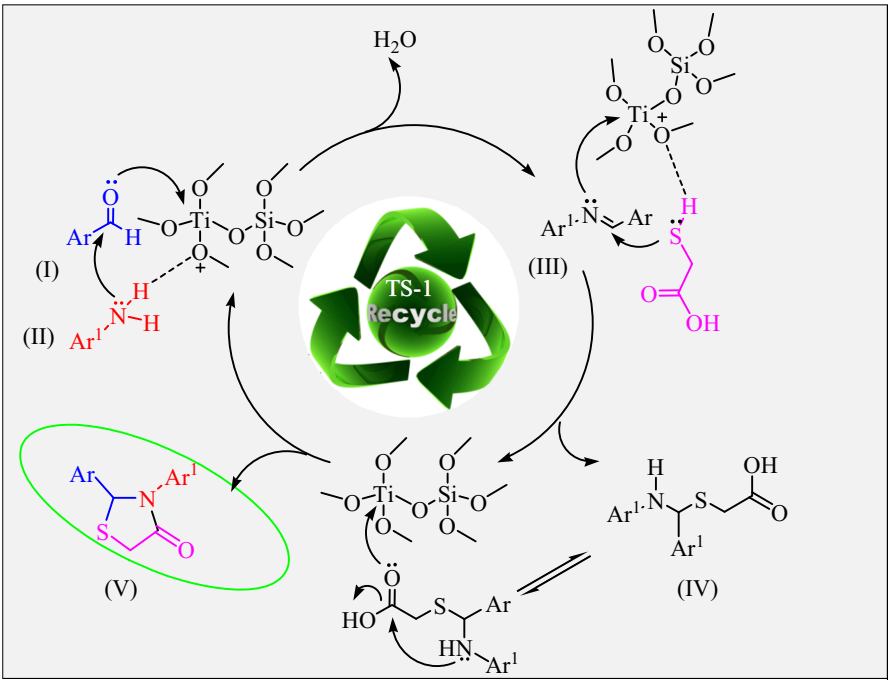


Fig. 4 Proposed reaction mechanism of 1,3-thiazolidin-4-ones in the presence TS-1 catalyst

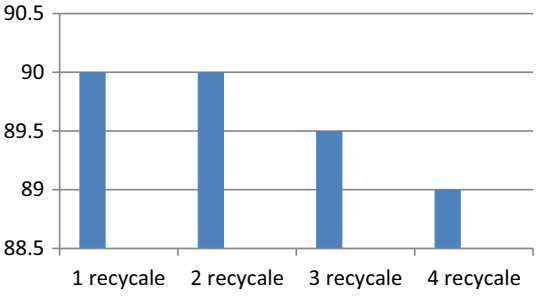


Fig. 5 Reusability test of TS-1 for synthesis of **3b**

Table 5 Catalytic performance of different reported catalysts for synthesis of **3b**

S. no.	Catalyst	Conditions (°C)	Time (min)	Yield (%)
1	MCM-41	110	720	97 [47]
2	$HClO_4$–SiO_2	PhMe/100	300	85 [48]
3	H_2SO_4–SiO_2	PhMe/100	300	55 [48]
4	TfOH–SiO_2	PhMe/100	300	72 [48]
5	$Bi[SCH_2COOH]_3$	70	30	75 [30]
6	TS-1	Solvent-free, 110	30	90 Our results

Catalyst activation and reusability

Catalysts were insoluble in solvent; therefore, easy to separate and recover by filtration. After completion of the reaction, catalysts were washed with acetone or any polar solvent to collect the catalyst, which was then dried at 105 °C under vacuum for 10 min. Reusability of the catalyst was also investigated for four successive reaction of model reaction and found that the catalyst has retained almost consistent activity. The catalyst was recycled (**3b** modal reaction) for four cycles without loss of catalytic activity (Fig. 5).

To specify the benefits of planned methodology, results of various reported strategies are compared with our results and are summarized in (Table 5). It was found that the TS-1 catalyst promotes reaction more effectively than different reported methodologies.

Conclusion

In the present study, synthesized Lewis acid catalyst TS-1 zeolite has highly Lewis and Bronsted acidic sides and excellent catalytic properties. Its catalytic potency was tested in one-pot solvent-free synthesis of 1,3-thiazolidin-4-ones via cyclic condensation of various aldehydes, aniline and thioglycolic acid. The present method offers remarkable advantages over reported methods such as the reusable nature of TS-1, non-toxicity, non-corrosive nature and excellent yield of 1,3-thiazolidin-4-ones, which makes the reaction more successful under environmental benign conditions.

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