Solid acid TS-1 catalyst: an efficient catalyst in Knoevenagel condensation for the synthesis of 5-arylidene-2,4-thiazolidinediones/Rhodanines in aqueous medium

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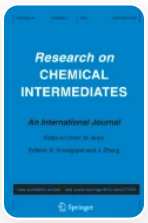

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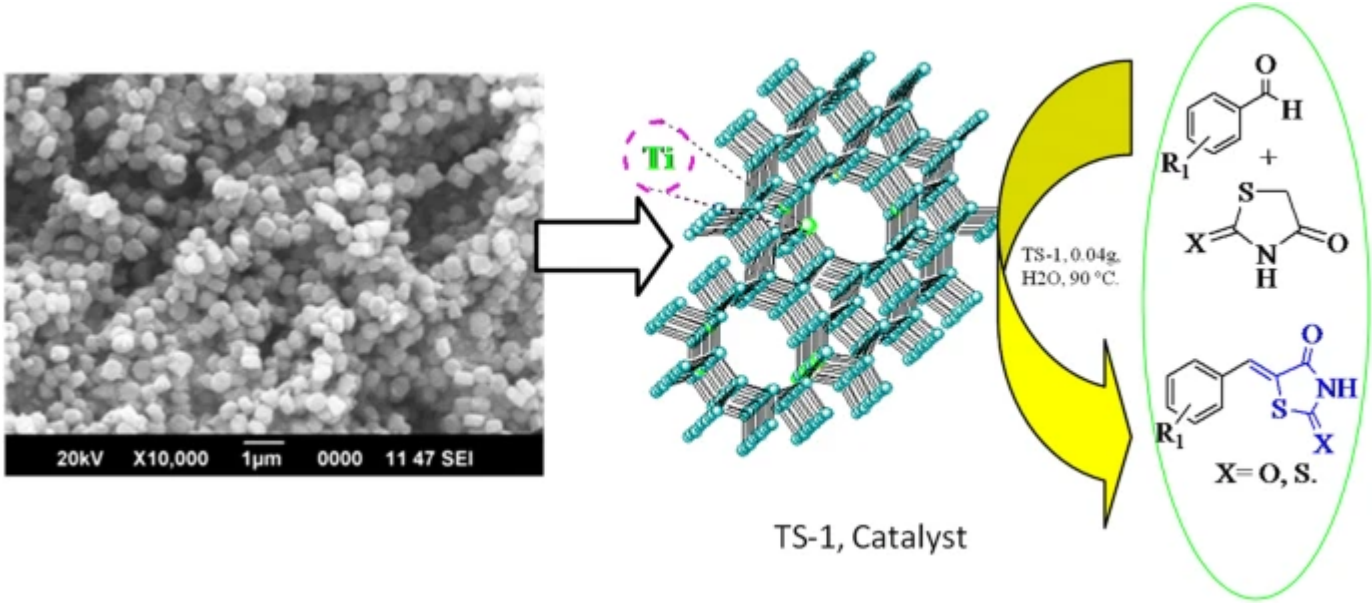
Sachin P. Gadekar, Sudarshan S. Dipake, Suresh T. Gaikwad & Machhindra K. Lande

Abstract

TS-1 zeolite was prepared for the synthesis of 5-arylidene-2,4-thiazolidinediones/Rhodanines in aqueous medium by incorporating titanium(IV) cations in a silicate-1 framework using hydrothermal treatment and characterized by using XRD, EDX, BET, FT-IR and SEM techniques. The catalytic activity of the catalyst

was tested for Knoevenagel condensation reaction. The condensation of active ethylene 2,4-thiazolidinedione with substituted aryl aldehydes under aqueous medium at 90 °C afforded the corresponding product in excellent yield up to 92% within 30 min. The present method offers several advantages over the reported methods such as easy separation of catalyst, simple work-up procedure, and an excellent yield of desired product. Furthermore, the catalyst could be reused without significant loss in activity.

Graphical abstract



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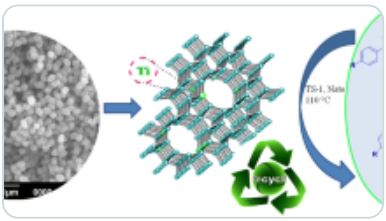

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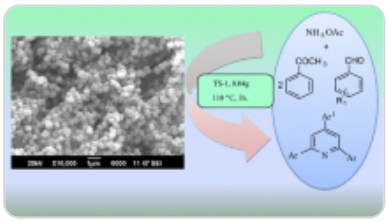

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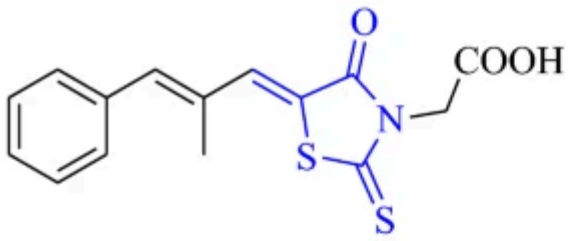
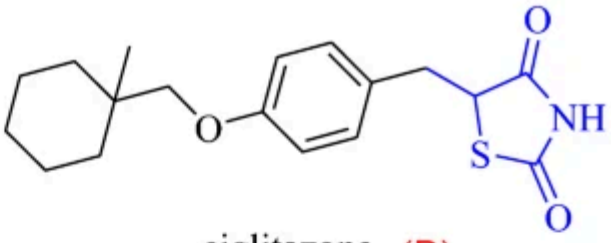
Introduction

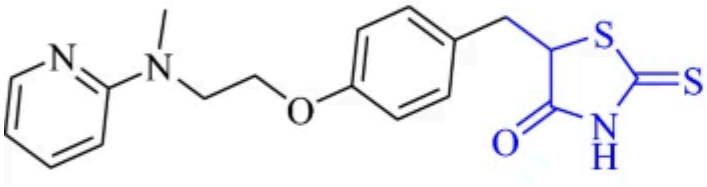
The majority of heterocyclic compounds present in most prescribed drugs presently marketed, having their intrinsic skillfulness and distinctive chemical properties have poised them as true cornerstones of medicinal chemistry. Thiazolidinedione/Rhodanines and other heterocyclic compounds containing Thiazolidinedione derivatives have attracted great attention due to their wide use as hypoglycemic/ant-diabetic (e.g., epalrestat A, ciglitazone B, and rosiglitazone C), antiapoptotic agents and functions as high-affinity PPARγ ligands [1,2,3]. The drugs having thiazolidinedione, moiety have increasing demand for pharmaceutical products, due to their wide range of biological activities such as antimicrobial, anti-bacterial [4,5,6,7], antifungal [8], anti-inflammatory [9, 10], antitubercular, anticancer agents [11,12,13], and polycystic ovary syndrome (POS) treatment [14], antiparasitic, and insecticidal activity [15]. It also shows an important application in DNA cleavage [16], particularly HIV-1 RT inhibitory [17,18,19,20], hypnotic [21], and anathematic agents [22].



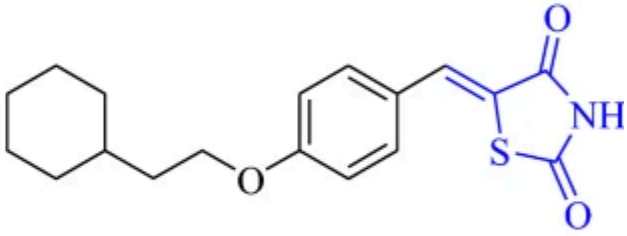
epalrestat (A)



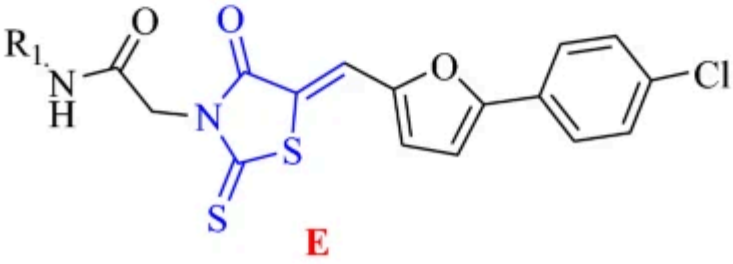
ciglitazone (B)



Rosiglitazone (C)



CT-8 (D)



E

Thiazolidinedione derivatives demonstrated for the solid anti-proliferative effect against human leukemia cells (E), tyrosine inhibitory activity [23,24,25], and also, 5-arylidene 4-thiazolidinediones derivatives found to be better antifungal agents than the parent 4-thiazolidinediones [26]. The methylene group at the fifth position in the 2,4-thiazolidinediones is more reactive, hence, most of the modifications have been carried out on the fifth position to build new molecules. A row of 5-arylidene-2,4-thiazolidinediones is under clinical trials as potential phospholipase A2 inhibitor, dual COX-2/5-LOX inhibitor [27]. In addition, thiazolidinedione based molecules have been popular as small molecule inhibitors such as aldose reductase [28]. As of late, 4-thiazolidinediones subordinates with antitumor movement for leukemia, lung, and melanoma, CNS, colon, renal, ovarian, prostate and bosom tumor cell lines have turned into a promising research area [11, 12]. Considering versatile applications of stated

heterocyclic compounds, several catalytic methods have been developed, such as CH_3COOH/CH_3COONa (12 h), CH_3COOH, CH_3COONa, $(CH_3CO)_2O$ [19, 20], pipyricine and acetic acid (10 h), hydroxyl ammonium ionic liquid [29], tetrabutylammonium hydroxide/H_2O–EtOH [30], alum [31], and aldonitrones in polyethylene glycol [32]. Although, reported methods are quite efficient but some of them suffer from one or the other drawbacks such as longer reaction time, harsh reaction conditions, use of volatile carcinogenic organic solvents, low yield and use of nonreusable and expensive catalysts, some methods require special conditions such as microwave and/or sonication in homogenous acids/bases, etc. [33, 34]. Hence, in order to overcome these limitations, we have developed and reported here in a strong Lewis acid; heterogeneous; solid acid TS-1 catalyst, and it has been reported that the TS-1 exhibits good catalytic activities in the epoxidation, oxidation, alkylation of phenol, and synthesis of 5-hydroxy-2(5H)-furanone [35,36,37,38,39]. It is sustainable, ecofriendly, efficient and a cost effective protocol for the synthesis of 5-arylidene-2,4-thiazolidinediones/Rhodanines.

Experimental

Preparation TS-1 catalyst

Solid acid catalyst, titanium silicate (TS-1), was prepared by using a reported method [40]. Titanium tetrabutoxide [$Ti(OBu)_4$] 1.16 ml was mixed in 30 ml of dry isopropyl alcohol, stirred vigorously for 10 min, Tetraethyl orthosilicate (TEOS) 24.37 ml and 20% tetrapropyl ammonium hydroxide (TPA-OH) 25 ml was added drop wise with vigorous stirring, resulting in a mixture that was stirred for 10 min at room temperature to obtain silica sol. Prepared titanium containing gel was added drop wise in silica sol with constant stirring at 70–75 °C, within 60–120 min. The basic pH of the gel was maintained by adding TPAOH and de-ionized water and the resulting gel mixture was transferred in an autoclave, under autogenously generated pressure at 175 °C for 24 h, and treated hydrothermally under static conditions. The solid product so obtained was filtered, dried at 100 °C for 1 h. and calcined at 500 °C for 4 h under air atmosphere. The subsequent material was cooled, portrayed and named as catalyst titanium silicate (TS-1).

General reaction procedure 5-arylidene-2,4-thiazolidinediones

The condensation of 2,4-thiazolidinedione/rhodaninediones (1 mmol), with aryl aldehydes (1 mmol), in the presence of a catalytic amount of TS-1 (0.04 g) in aqueous medium at 90 °C was carried out by refluxing the reaction mixture for 30–60 min to obtain 5-arylidene-2,4-thiazolidinediones/Rhodaninediones derivatives, as shown in

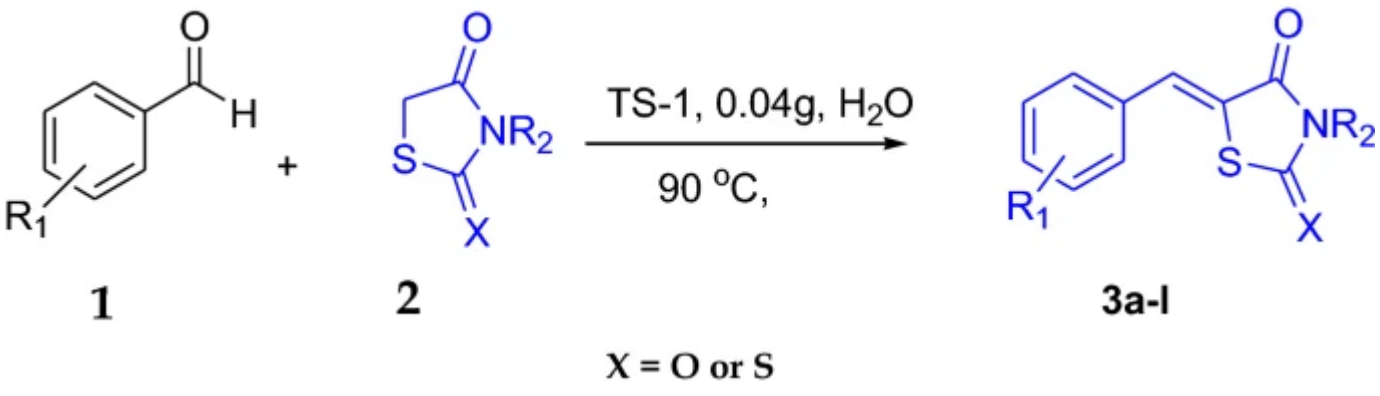
Table 2, which afforded the corresponding products in excellent yields up to 92% within 30 min. Active methylene thiazolidinedione was prepared by using a reported method [41]. The progress of the reaction was monitored by thin layer chromatography using PET ether: ethyl acetate (8:2) as a solvent system. After completion of the reaction, the reaction mixture was filtered to recover the catalyst TS-1. The filtrate was concentrated to obtain crude product, which was recrystalized from hot ethanol to obtain pure product (2a–i).

Results and discussion

The -CHO group can be transformed to a 5-aryl thiazolidinedione skeleton by the reaction of aldehyde and thiazolidinediones in the presence of TS-1 catalyst. Where, TS-1 was utilized as a Lewis acid as well as a dehydrating agent to accelerate the intermolecular condensation, resulting in faster reaction and improved product yield. To find optimum loading of catalyst amount and suitable reaction conditions, aryl benzaldehyde (1 mmol), was allowed to react with 2,4 thiazolidinedione (1 mmol) as model reaction 3c with 0.04 g TS-1 as a catalyst in various solvents; reflux conditions and results are summarized in Table 1. In the absence of catalyst, the reaction does not proceed to give the product (3c) even after 60 min, Table 3. However, the same reaction, when carried out with different amounts of TS-1 catalyst under reflux conditions, has been found to give a reaction with an excellent yield of product (3c), which indicates a crucial role of TS-1 catalyst in the completion of reaction (Scheme 1).

Table 1 TS-1 catalyzed synthesis of 5-aryl thiazolinedione derivatives

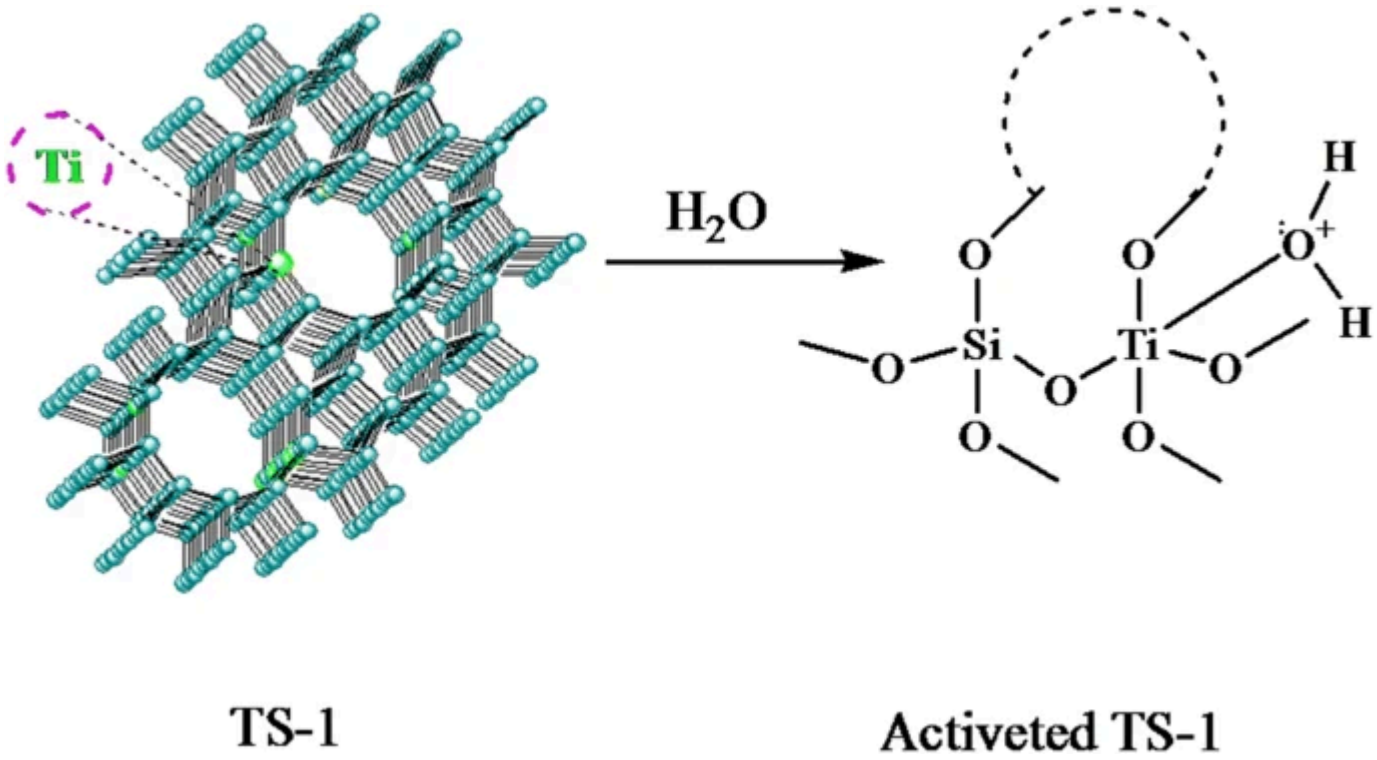
Scheme 1



Synthesis of 5-aryl thiazolinedione skeleton derivatives

In order to investigate the scope and importance of the present method, substituted benzaldehydes and 2,4-thiazolidinedione were refluxed under optimum reaction conditions, and it is observed that there is no significant adverse effect on the yield of corresponding 5-arylidene-2,4-thiazolidinedione for different substituted benzaldehyde in a stipulated time (Fig. 1).

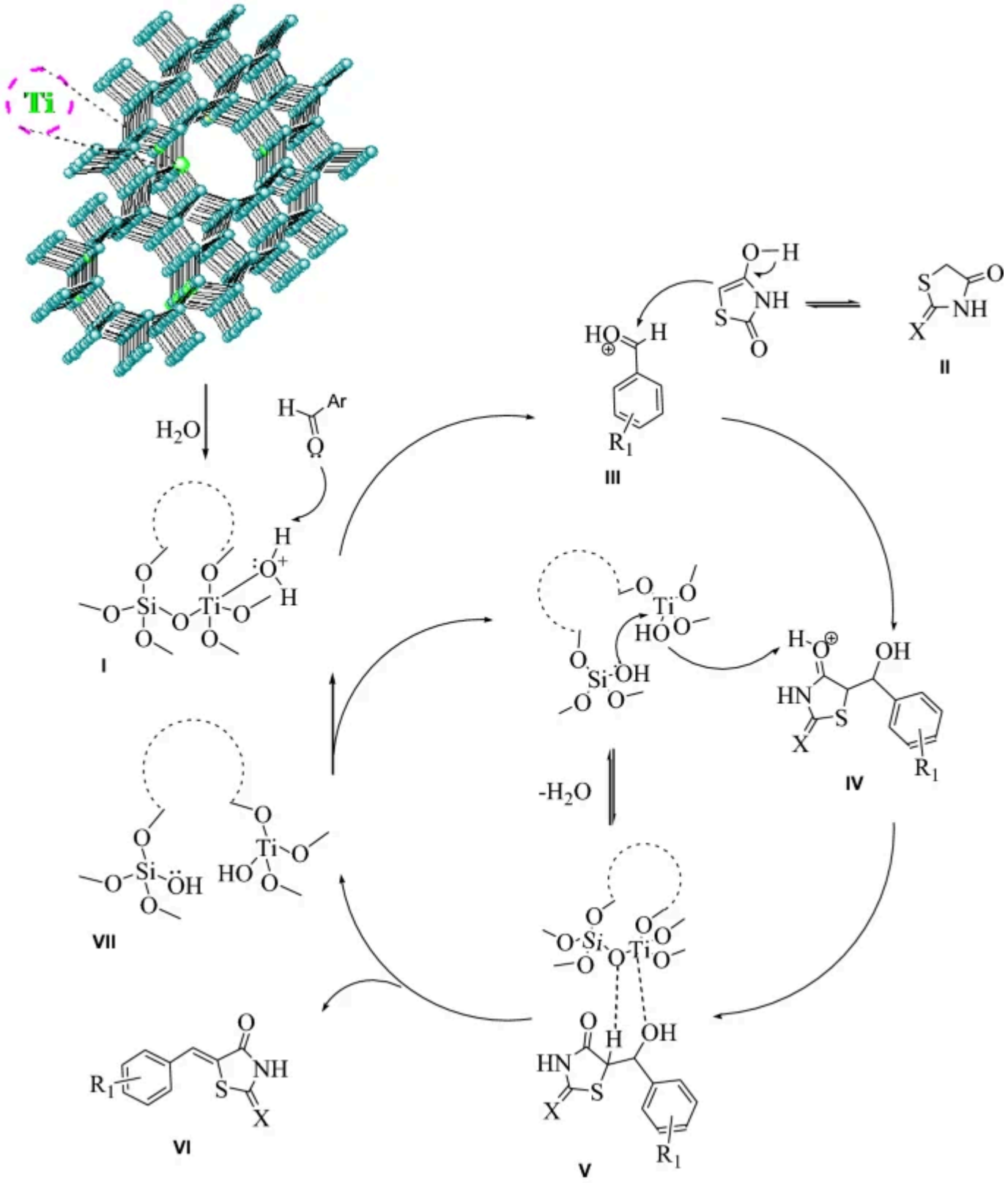
Fig. 1



Catalyst activation

The catalyst was separated, washed with acetone and activated by drying at 120 °C for 10 min, before the next catalytic run. Reusability of the catalyst was investigated three times, and it was found that the catalyst has retained almost consistent activity (Table 1, entry 3c; Fig. 2).

Fig. 2



Cyclic mechanism

Optimization of reaction conditions

In order to confirm the optimum loading amount of TS-1 catalyst, a variable amount of catalyst were used for the model reaction, and the results are summarized in Table 2. In synthesis, aryl aldehyde (1 mmol), 2,4-thiazolidinedione/Rhodanine (1 mmol) was used

and refluxed with TS-1 (0.04 g) catalyst. Initially, several protic and aprotic solvents with appropriate time and temperature were screened and the obtained results are summarized in Table 3 (model reaction 3c). It has been found that in the absence of a catalyst the reaction did not give satisfactory results of the desired product in a stipulated time, however, reaction yield is maximum in aqueous solvent. Therefore, further optimization of catalyst was performed in aqueous medium. It has been found that the 0.04 g, TS-1 catalyst is sufficient for model reaction (3c, Table 1), furthermore, temperature and time were also optimized, Table 3. Catalytic performances of TS-1 catalyst was compared with another reported method, Table 4.

Table 2 Effect of the amount of TS-1 on model reaction 3c

Table 3 Effect of various solvents in the presence of TS-1 catalyst on model reaction 3c

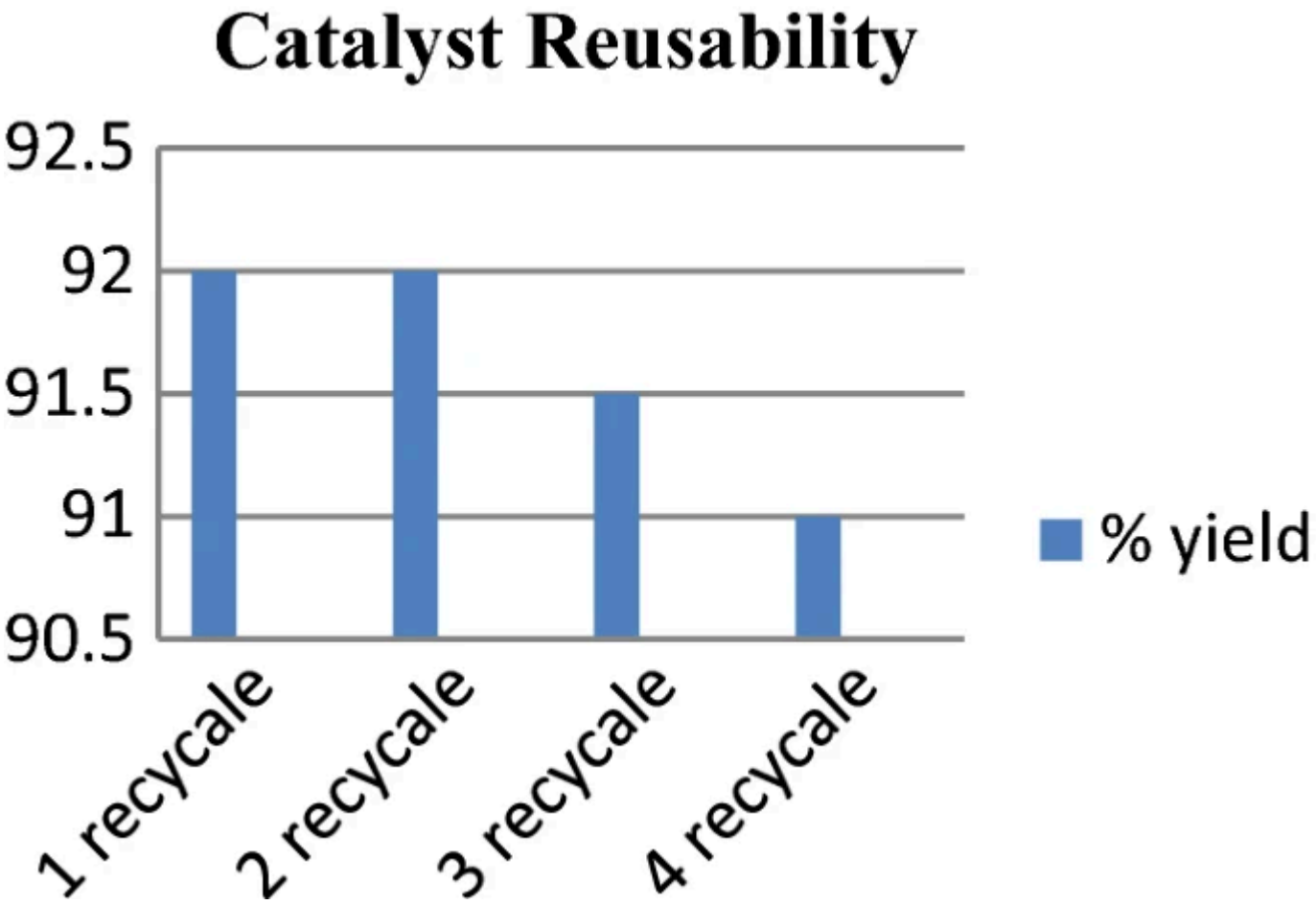
Table 4 Catalytic performance of reported catalysts for the synthesis of 3c

In order to explore the scope and importance of the proposed method, with the optimized conditions for TS-1, it was tested for the synthesis 5-aryl thiazolidinedione derivatives; results summarized in Table 1.

Catalyst activation and reusability

Solid TS-1 catalyst is insoluble in most of the solvents, therefore, it is easy to separate from reaction mixture and recovered by simple filtration, and recovered catalyst was washed with acetone or any polar solvent and activated at 105 °C under vacuum for 10 min. Reusability of catalyst was further investigated for four successive model reactions, and iit was found that the catalyst has retained almost consistent activity (Fig. 3).

Fig. 3



Reusability test of TS-1 for the synthesis of **3c**

Conclusions

We have developed a straightforward, rapid, and environmentally benign protocol for the synthesis of 5-arylidine-2,4-thiazolidinediones and 5-arylidne-Rhodanines via titanium silicate (TS-1) zeolite catalyzed Knoevenagel reaction. It gives excellent yield, catalytic potency and number of synthetic features, activating both reactants without the formation of any complexes/by-products, with 92% yields in shorter reaction time. The used catalyst activation is very simple; just calculation at 105 °C for 10 min and then recycled four times without much reduction in catalytic activity. These features make the present protocol more innovative than existing ones. This work will contribute a lot for further development for the titanium silicate TS-1 solid acid zeolite as catalyst.

References

1. P.A. Datar, S.B. Aher, J. Saudi Chem. Soc. **20**, S196 (2016)

Article CAS Google Scholar

2. K.D. Patel, C.N. Patel, G.M. Patel, Med. Chem. (Los Angeles) **6**(10), 647 (2016)

Article Google Scholar

3. R.S. Bhatti, S. Shah, Suresh, P. Krishan, J.S. Sandhu, Int. J. Med. Chem. 793260 (2013)

4. K.R. Alagawadi, S.G. Alegaon, Arab. J. Chem. **4**, 465 (2011)

Article CAS Google Scholar

5. B. Bozic, J. Rogan, D. Poleti, M. Rancic, N. Trisovic, B. Bozic, G. Uscumlic, Arab. J. Chem. **10**, S2637 (2017)

Article CAS Google Scholar

6. N. Trotsko, A. Przekora, J. Zalewska, G. Ginalska, A. Paneth, M. Wujec, J. Enzyme Inhibid. Med. Chem. **33**, 17 (2017)

Article Google Scholar

7. O. Zvarec, S.W. Polyak, W. Tieu, K. Kuan, H. Dai, D.S. Pedersen, R. Morona, L. Zhang, G.W. Booker, A.D. Abell, Bioorg. Med. Chem. Lett. **22**, 2720 (2012)

Article CAS Google Scholar

8. E. Valadbeigi, S. Ghodsi, Med. Chem. (Los Angeles) **7**(6), 178 (2017)

Article Google Scholar

9. Sucheta, S. Tahlan, P.K. Verma, Chem. Cent. J. **11**, 130 (2017)

Article CAS Google Scholar

10. L.F. Junior, M.J.B. Rego, M.B. Cavalcanti, M.C. Pereira, M.G. Pitta, P.S.S. Oliveira, S.M.C. Gonçalves, A.L.B.P. Duarte, M.C.A. Lima, I. Pitta, M.G. Pitta, BioMed Res. Int. 926060 (2013)

11. A.C. Tripathi, S. Gupta, G. Fatima, P.K. Sonar, A. Verma, S.K. Saraf, Eur. J. Med. Chem. **72**, 52e77 (2014)

Article Google Scholar

12. D.D. Subhedar, M.H. Shaikh, L. Nawale, A. Yeware, D. Sarkar, B.B. Shingate, Res. Chem. Intermed. **42**, 6607 (2016)

Article CAS Google Scholar

13. M. Azizmohammadi, M. Khoobi, A. Ramazani, S. Emami, A. Zarrin, O. Firuzi, R. Miri, A. Shafiee, Eur. J. Med. Chem. **59**, 15e22 (2013)

Article Google Scholar

14. D. Glintborg, M. Andersen, Gynecol. Endocrinol. **26**(11), 791 (2010)

Article CAS Google Scholar

15. A.P. Rauter, M. Padilha, J.A. Figueiredo, M.I. Ismael, J. Justino, H. Ferreira, M.J. Ferreira, C. Rajendran, R. Wilkins, P.D. Vaz, M.J. Calhorda, J. Carbohydr. Chem. **24**, 275 (2005)

Article CAS Google Scholar

16. S.V. Laxmi, P. Anil, G. Rajitha, A.J. Rao, P.A. Crooks, B. Rajitha, J. Chem. Biol. **9**, 97 (2016)

Article Google Scholar

17. S. Ozkirimli, F. Kazan, Y. Tunali, J. Enzyme Inhibid. Med. Chem. **24**(2), 447 (2009)

Article CAS Google Scholar

18. R.S. Bahare, S. Ganguly, K. Choowongkomon, S. Seetaha, DARU J. Pharm. Sci. **23**(6), 1 (2015)

Google Scholar

19. S. Chandrappa, S.B. Benaka Prasad, K. Vinaya, C.S. Ananda Kumar, N.R. Thimmegowda, K.S. Rangappa, Investig. New Drugs **26**, 437 (2008)

Article CAS Google Scholar

20. J. Dolezel, P. Hirsova, V. Opletalova, J. Dohnal, V. Marcela, J. Kunes, J. Jampilek, Molecules **14**, 4197 (2009)

Article CAS Google Scholar

21. N. Ergenc, G. Capan, N.S. Gunay, S. Ozkirimli, M. Gungor, S. Ozbey, E. Kendi, Arch. Pharm. **332**(10), 343 (1999)

Article CAS Google Scholar

22. H. Sachdeva, D. Dwivedi, P. Goyal, Org. Chem. Int. 976032 (2013)

23. Y. Wu, H. Tai, H. Cho, Bioorg. Med. Chem. **18**, 1428 (2010)

Article CAS Google Scholar

24. S. Chandrappa, C.V. Kavitha, M.S. Shahabuddin, K. Vinaya, C.S.A. Kumar, S.R. Ranganatha, S.C. Raghavan, K.S. Rangappa, Bioorg. Med. Chem. **17**, 2576 (2009)

Article CAS Google Scholar

25. Y. Mi Ha, Y.J. Park, J. Kim, D. Park, J.Y. Park, H. Jin Lee, J.Y. Lee, H.R. Moon, H.Y. Chung, Eur. J. Med. Chem. **49**, 245 (2012)

Article Google Scholar

26. Y. Zhang, Z. Zhou, Org. Chem. Int. 194784 (2012)

27. S. Rathod, M. Navgire, B. Arbad, M. Lande, S. Afr. J. Chem. **65**, 196 (2012)

CAS Google Scholar

28. G. Bruno, L. Costantino, C. Curinga, R. Maccari, F. Monforte, F. Nicolo, R. Ottana, M.G. Vigorita, Bioorg. Med. Chem. **10**(4), 1077 (2002)

Article CAS Google Scholar

29. J. Zhang, Y. Zhang, Z. Zhou, Green Chem. Lett. Rev. **7**(1), 90 (2014)

Article Google Scholar

30. A. Khazaei, H. Veisi, M. Safaei, H. Ahmadian, J. Sulfur Chem. **35**(3), 270 (2014)

Article CAS Google Scholar

31. K.F. Shelke, S.B. Sapkal, G.K. Kakade, S.A. Sadaphal, B.B. Shingate, M.S. Shingare, Green Chem. Lett. Rev. **3**, 17 (2010)

Article CAS Google Scholar

32. D. Kumar, S. Narwal, J.S. Sandhu, Int. J. Med. Chem. 273534 (2013)

33. Suresh, J.S. Sandhu, Org. Med. Chem. Lett. **3**, 2 (2013)

Article CAS Google Scholar

34. K.F. Shelke, A.D. Badar, J.B. Devhade, Chem. Biol. Interface **6**(6), 410 (2016)

CAS Google Scholar

35. Z. Zhuo, L. Wu, L. Wang, Y. Ding, X. Zhang, Y. Liu, M. He, RSC Adv. **4**, 55685 (2014)

Article CAS Google Scholar

36. S.B. Shin, D.W. Lee, D. Chadwick, J. Mol. Catal. A Chem. **423**, 478 (2016)

Article CAS Google Scholar

37. A.S. Albero, A.G. Atienza, E. Serrano, J.G. Martínez, J.S. Albero, Catal. Commun. **44**, 35 (2014)

Article Google Scholar

38. D. Vitvarov, L. Lupínkov, M. Kub, Microporous Mesoporous Mater. **210**, 133e141 (2015)

Google Scholar

39. P. Kumar, R.K. Pandey, Green Chem. **2**, 29 (2000)

Article CAS Google Scholar

40. S. P. Gadekar, G. T. Pawar, R. R. Magar, M. K. Lande, Polycycl. Aromat. Compd. (2017). https://doi.org/10.1080/10406638.2017.1363060

Article Google Scholar

41. N. Sachan, S.S. Kadam, V.M. Kulkarni, Indian J. Heterocycl. Chem. **17**, 57 (2007)

CAS Google Scholar

42. L.S. Gadekar, B.R. Arbad, M.K. Lande, Org. Chem. Indian J. **4**, 458 (2008)

Google Scholar

43. R.S. Mahalle, P.D. Netankar, S.P. Bondge, R.A. Mane, Green Chem. Lett. Rev. **1**, 103 (2008)

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