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Graphical Abstract

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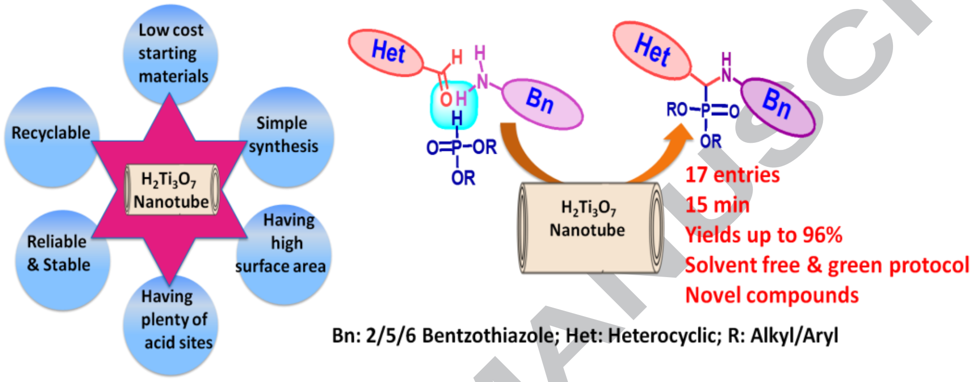

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Protonated trititanate nanotubes: An efficient catalyst for one-pot three-component coupling of benzothiazole amines, heterocyclic aldehydes and dialkyl/diaryl phosphites with a greener perspective

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ABSTRACT

Nano-size catalysts of TiO_2, ZnO, CuO and protonated trititanate nanotubes ($H_2Ti_3O_7$) have been investigated for the one-pot three component synthesis of novel α-aminophosphonates from benzothiazole amines, heteroaldehydes and dialky/diaryl phosphites via Kabachnik-Fields reaction. This methodology provides a new and convenient approach to multicomponent reaction and the $H_2Ti_3O_7$ nanotubes catalyst is recyclable upto seven cycles.

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1. Introduction

In recent years, nano-catalysis has emerged as a sustainable and competitive alternate to conventional catalysis since the nanoparticles (NPs)/nanostructers (NS) possess selectivity and reactivity, while at the same time maintain the intrinsic features of a heterogeneous catalyst. The ease of separation, recovery and reuse of these NPs/NS further enhance their attractiveness as green and sustainable catalysts.[1] Among various nanostructured materials, the TiO_2 nanostructures have been widely investigated over the past few decades due to multiple potential applications in Friedel-Crafts alkylation,[2a-d] Michael reaction,[2e] Biginelli condensation,[2f] Strecker reaction,[2g] Kabachinick-Fields reaction,[2h] synthesis of 5-hydroxymethyl-furfural,[2i] α-hydroxy phosphonates,[2j] nucleic bases,[2k] multi component synthesis of 2-oxo dihydropyrroles[2l] and polysubstituted pyrrolidinones.[2m]

Now a days, one dimensional (1-D) TiO_2 nanotubes, nanorods and nanowires attracted much attention due to their unique properties *viz.*, large surface-to-volume ratio, better dispersibility, decreased inter-crystalline contacts and increased accessibility of acid sites.[2a-c &3] In this connection, we succeeded in synthesis of tertiary α-aminophosphonates through the catalytic application of $H_2Ti_3O_7$ nanotubes (TNT) and nanorods (TNR) with high yields.[4]

The synthesis of α-aminophosphonates have witnessed tremendous growth due to broad spectrum of biological and pharmaceutical properties such as anticancer,[5a-c] antileishmanial chemo type,[5d] antiproliferative,[5e] antioxidant,[5f] antimicrobial,[5g, 5h] antiviral[5i] activities and inhibitors of protein tyrosine phosphatases.[5j] Owing to the potential importance of α-aminophosphonate derivatives in life sciences, pharmaceuticals and agriculture; world-wide efforts have been made in the last few decades by researchers and various protocols have been developed for their synthesis using various Brønsted/Lewis acids, heteropoly acids and heterogeneous catalysts.[6] But, some of the methodologies endure few setbacks such as unavailable starting materials, usage of corrosive catalysts, multi step process, high temperature, long reaction time, non-compatible solvent and low yields. Moreover several research groups focused on the synthesis of α-aminophosphonates using simple aromatic amines/aldehydes and phosphites, but limited with heterocyclic amines/aldehydes and phosphites. Hence, the development of simple, effective, high-yielding and environmentally friendly approaches using new catalysts for the synthesis of heterocycle derived α-aminophosphonates is an important task for organic chemists. Among various heterocycles known benzothiazole skeleton is considered to be the most "privileged" structure due to its biological and pharmaceutical properties.[7]

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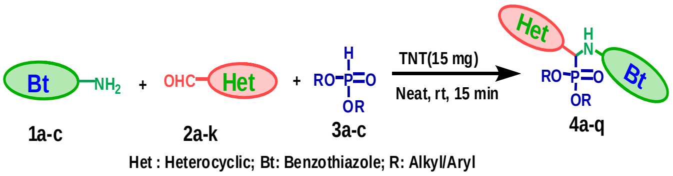
In continuation of our research interest on the introduction of recoverable TNT catalysts, we surmised that novel benzothiazole derived α-aminophosphonates (**4a-q**) (**Scheme 1**) can be synthesized from 5/6-aminobenzothiazoles with various heterocyclic aldehydes and dialkyl/diaryl phosphites *via* Kabachnik-Fields reaction in the presence of environmentally benign, easily separable, recyclable, and highly effective catalyst system TNT. Further the reaction conditions like optimization of catalyst and solvent were carried out and listed in **Fig. 1** and **Table .2**



Scheme 1. TNT catalyzed Kabachnik-Fields reaction of benzothiazole amines, different heterocyclic aldehydes and dialky/diaryl phosphites.

2. Results and discussion

2.1. Catalytic activity of TNT

The catalytic performance of the TNT was examined through Kabachnik-Fields reaction of benzo[*d*]thiazol-5-amine (**1b**), 5-methoxybenzofuran-2-carbaldehyde (**2a**) and diphenyl phosphite (**3c**) in toluene at room temperature, which afforded diphenyl (benzo[*d*]thiazol-5-ylamino)(5-methoxybenzofuran-2-yl)methyl-phosphonate (**4d**). For comparison of the results, we tested the catalytic activity using commercially available material such as bulk/nano TiO_2 as well as nano ZnO and nano CuO. The formation of **4d** was observed with all the catalysts (**Fig. 1**). In the case of bulk TiO_2, the yields of **4d** did not reach 25% even after 30 min. While in the case of nano TiO_2, nano ZnO and nano CuO the results were obtained in moderate yields. In contrast to the bulk/nano TiO_2, nano ZnO and nano CuO; TNT exhibited remarkable catalytic performance. However, the reaction did not occur in the absence of the catalyst even with prolonged reaction time (Table 2, Entry 8).

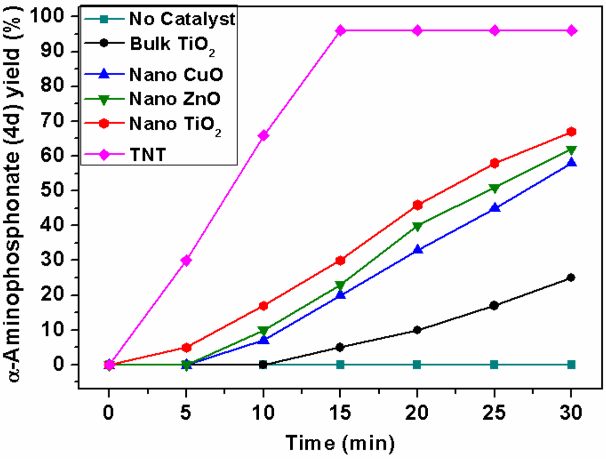


Fig.1 Time courses of α-aminophosphonate (**4d**) formation using various solid acid catalysts.

Reaction conditions: Catalyst (15 mg), benzo[*d*]thiazol-5-amine (1 mmol), 5-methoxybenzofuran-2-carbaldehyde (1 mmol), diphenyl phosphite (1 mmol), toluene (1 mL) and at room temperature.

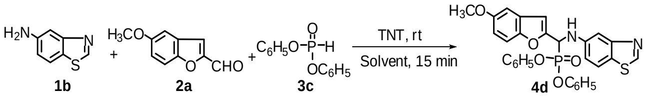
To understand the reason behind the remarkable activity of TNT over the other samples used, we investigated acidity of the catalysts using NH_3-TPD (**Table 1**). In NH_3-TPD test TNT showed greater desorption of NH_3 over bulk/nano TiO_2, nano CuO and nano ZnO. Therefore, the outstanding activity of TNT over the other samples tested may be due to the increased acidity. Besides this, higher surface area and porous nature of TNT may also contribute to its catalytic performance.

Table 1. NH_3 adsorption capacities equal to total amounts of acid sites.

Entry	Catalyst	Amount of acid sites ($mL.g^{-1}$ of NH_3)[Ref]
1	Nano CuO	14.5[2e]
2	Nano ZnO	15.6[2e]
3	Bulk TiO_2	0.1[2e]
4	Nano TiO_2	16.2[2e]
5	TNT	84.6

As far as the effect of solvent concerned, the model reaction was carried out in several solvents as well as solvent free condition to investigate the efficiency of the catalyst. From **Table 2**, it is evidenced that the best yield was obtained when the reaction was performed in toluene. It is quite interesting to note that the reaction also took place smoothly under solvent free conditions and generated the corresponding α-aminophosphonate in excellent yield. To avoid the use of volatile solvents and to reduce the environmental hazards, all the three-component coupling reactions were performed under solvent free conditions. Further investigation revealed that the result was affected by the amount of catalyst. The catalyst loading varied from 5 to 20 mg and observed that maximum yield obtained with just 15 mg. However no significant improvement in yield was observed when the catalyst load is increased to more than 15 mg.

Table 2. Screening of reaction conditions for the synthesis of α-aminophosphonate (**4d)** by TNT catalyst



Entry	Solvent	Catalyst loading (mg)	Yield[a] (%)
1	Toluene	15	96
2	Ethanol	15	50
3	DMSO	15	10
4	DMF	15	15
5	Acetonitrile	15	75
6	Water	15	0
7	Neat	15	95
8[b]	Neat	---	---
9	Neat	5	68
10	Neat	10	82
11	Neat	12.5	90
12	Neat	17.5	95
13	Neat	20	95

Reaction conditions: Benzo[*d*]thiazol-5-amine (1 mmol), 5-methoxybenzofuran-2-carbaldehyde (1 mmol), diphenyl phosphite (1 mmol), solvent (1 mL), TNT catalyst, r.t and quenched after 15 min. [a] Isolated yield. [b] Reaction continued up to 6 h.

Under optimal conditions, we chose a variety of structurally different benzothiazole amines heterocyclic aldehydes, and dialkyl/diaryl phosphites to understand the scope and efficiency of the TNT promoted one-pot three component Kabachnik-Fields reaction and the results are compiled in **Table 3**. The reaction of benzo[*d*]thiazol-6-amine (**1a**), 5-methoxybenzofuran-2-carbaldehyde (**2a**) and dialkyl/diaryl phosphites (**3a-c**) was carried out to determine the influence of the phosphite. In case of

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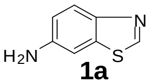
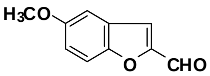
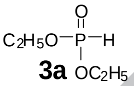
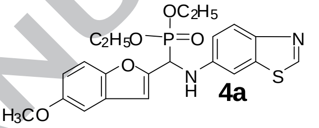
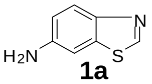
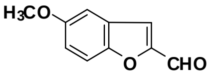
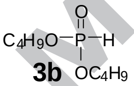
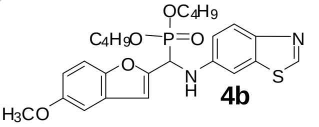
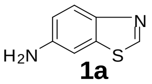
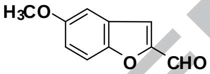
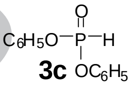
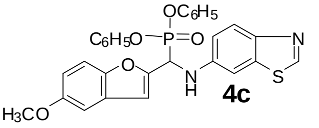
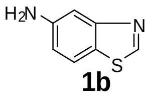
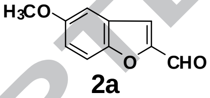
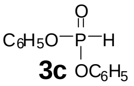
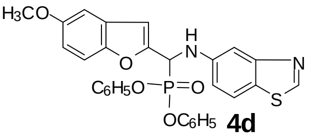
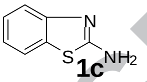
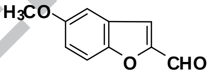
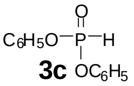
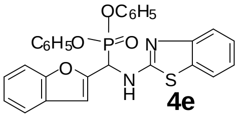
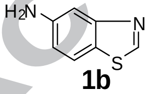
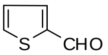
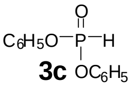
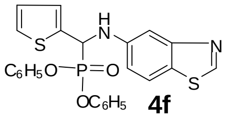
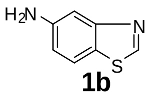
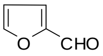
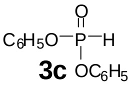
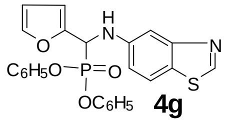
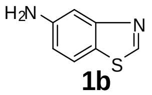
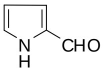
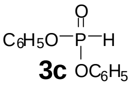
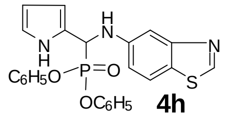
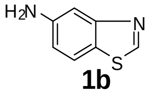
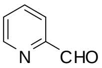
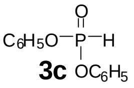
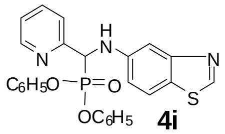
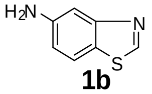
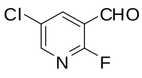
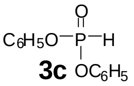
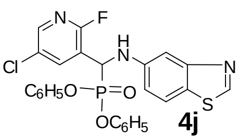
dialkyl phosphites, the yield was decreased with increase in the alkyl chain (**4a-b**). Diphenyl phosphite gave better yield than dialkyl phosphites and moreover the products obtained as solids while brown colour oils were observed with dialkyl phosphites. We then selected benzo[*d*]thiazol 2/5/6 amines, instead of simple aromatic amines to carry out the reaction. Benzo[*d*]thiazol-5-amine (**1b**) afforded better yield when compare to benzo[d]thiazol-6-amine (**1a**), on the other hand benzo[d]thiazol-2-amine (**1c**) was found to be ineffective partner in this three-component reaction. To expand the scope of aldehyde substrates, we studied the reaction with a variety of heterocyclic aldehydes. In all the cases, the corresponding α-aminophosphonates were obtained in good to excellent yields except with 1*H*-pyrrole-2-carbaldehyde (**2d**) and 1*H*-imidazole-4-carbaldehyde (**2k**). Thiophene-2-carbaldehyde (**2b**) was a better substrate than furan-2-carbaldehyde (**2c**) in the case of simple 5-membered heterocycles for this coupling reaction. 2,6-Dimethoxynicotinaldehyde (**2g**) afforded superior yield than 5-chloro-2-fluoronicotinaldehyde (**2f**) in nicotinaldehyde series. 1*H*-Indole-3-carbaldehyde (**2h**) gave low yield i.e 79% due to its less solubility. The remaining aldehydes 5-methoxybenzofuran-2-carbaldehyde (**2a**), picolinaldehyde (**2e**), 2-cyclopropylpyrimidine-4-carbaldehyde (**2i**) and 3-(pyrimidin-5-yl)benzaldehyde (**2j**) gave the promising yields. All products were characterized by IR, NMR (^{1}H, ^{13}C & ^{31}P) and mass spectral (HRMS) analysis, which for known compounds were found to be identical with the literature data (**4m, 4q**)[6a] and the remaining new compounds were analysed spectroscopically and described in the supporting information. The *NH* protons were confirmed by D_2O exchange experiments. It is of quite interest to observe the *NH* proton resonating at 5.00-4.96 ppm as quartet as seen in proton NMR of **4d** and its disappearance was found in D_2O exchange experiments.

Table 3. TNT catalyzed synthesis of α-aminophosphonates (**4a-q**)

Entry	Amine (**1a-c**)	Aldehyde (**2a-k**)	Phosphite (**3a-c**)	Product (**4a-q**)	Yield[a] (%)
1	 **1a**	 **2a**	 **3a**	 **4a**	84
2	 **1a**	 **2a**	 **3b**	 **4b**	80
3	 **1a**	 **2a**	 **3c**	 **4c**	90
4	 **1b**	 **2a**	 **3c**	 **4d**	95
5	 **1c**	 **2a**	 **3c**	 **4e**	0
6	 **1b**	 **2b**	 **3c**	 **4f**	95
7	 **1b**	 **2c**	 **3c**	 **4g**	89
8	 **1b**	 **2d**	 **3c**	 **4h**	0
9	 **1b**	 **2e**	 **3c**	 **4i**	95
10	 **1b**	 **2f**	 **3c**	 **4j**	81

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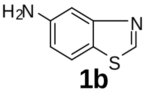
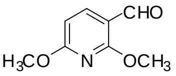
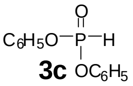
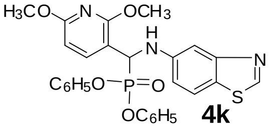
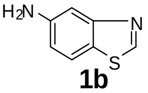
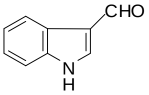
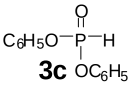
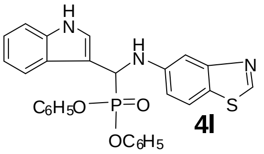
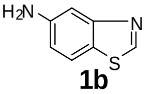
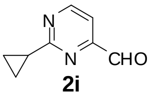
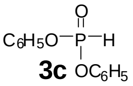
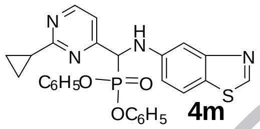
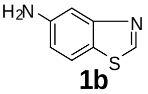
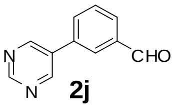
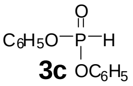
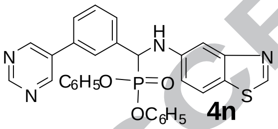
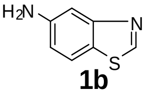
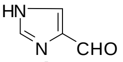
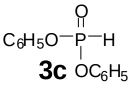
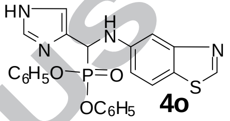
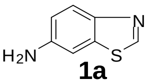
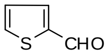
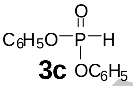
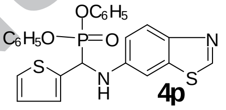
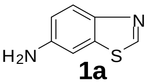
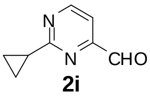
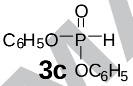
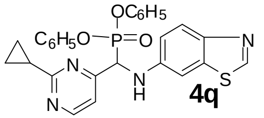
11	 **1b**	 **2g**			89
12	 **1b**	 **2h**			79
13	 **1b**	 **2i**			90
14	 **1b**				96
15	 **1b**	 **2k**			trace
16	 **1a**	 **2b**			88
17	 **1a**	 **2i**			90

Reaction conditions: Benzothiazole amine (1 mmol), heterocyclic aldehyde (1 mmol), dialkyl/diaryl phosphite (1 mmol), solvent free, r.t and 5 mol% TNT catalyst quenched after 15 min. [a] Isolated yields

From these results, plausible mechanism is proposed for the process of TNT catalyzed Kabachnik-Fields reaction (**Fig. 2**). The mechanism involves the activation of aldehyde by TNT (**I**) followed by the nucleophilic addition of amine to afford imine (**II**) and the subsequent activation of imine (**II**) by TNT facilitates the addition of phosphite to give an activated phosphonium intermediate (**III**), which then gave the desired product **(IV)** (**Fig. 2**). The acid-base interaction between the TNT-aldehyde (in imine formation step) and TNT-imine (in phosphite addition step) facilitated the reaction by shifting the equilibrium towards product formation.

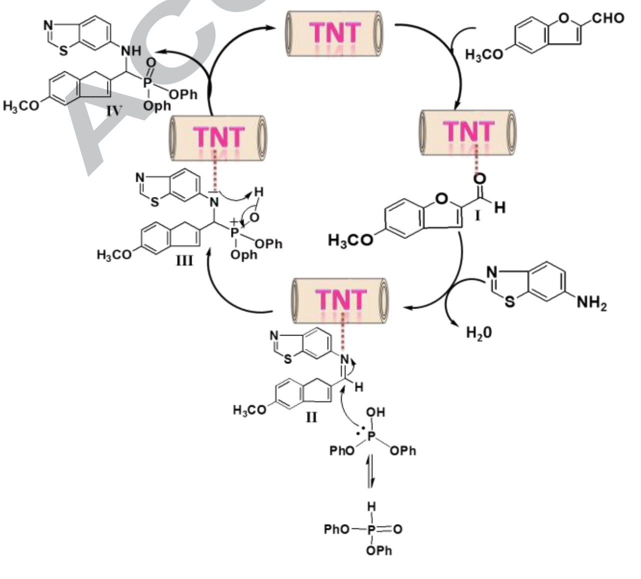


Fig. 2 A possible mechanism for the synthesis of α-aminophosphonates over a TNT catalyst.

Encouraged by the highly efficient catalytic outcome of TNT as depicted in **Table 4**, we tested its ability to perform as a recyclable catalyst with the coupling reaction of benzo[*d*]thiazol-5-amine (**1b**), 5-methoxybenzofuran-2-carbaldehyde (**2a**) and diphenyl phosphite (**3c**). After each catalytic cycle, the reaction mixture was dissolved in EtOAc (2mL) and the catalyst was separated by centrifugation, thoroughly washed with EtOAc and finally dried at 100 °C for 6 h before performing the next cycle. We checked the recyclability test up to seven consecutive cycles and examined that first four cycles resulted in quantitative yields of **4d** without any loss of catalytic efficiency, however, from the 5th cycle onwards a slight decrease of catalytic efficiency was observed (**Table 4**).

To understand the reason behind decrease in catalytic efficiency, we carried out the NH_3-TPD experiment for fresh and reused TNT (after 7th cycle) to determine acid sites concentration. The NH_3-TPD curve (**Fig. 3**) of the fresh and reused TNT sample consists of two unresolved peaks (at around 160.9 and 302 °C for fresh TNT; at around 148.5 and 294.3 °C for reused TNT). The low and high temperature peaks could be attributed to NH_3 desorbtion from weak and strong acidic sites, respectively.[8] The total amount of NH_3 adsorption on fresh and reused TNT is 84.6 $mL.g^{-1}$ and 52.2 $mL.g^{-1}$, respectively. The decrease in concentration of acid sites may be one of the main reasons for the drop in yield of the product.

Table 4. Recyclability studies of TNT on the synthesis of α-aminophosphonate (**4d**)

Run	1	2	3	4	5	6	7
Yield[a](%)	95	95	95	95	93	88	81

Reaction conditions: Benzo[*d*]thiazol-5-amine, (1 mmol) 5-methoxybenzofuran-2-carbaldehyde (1 mmol) and diphenyl phosphite (1 mmol), solvent free, TNT catalyst (15 mg), r.t and quenched after 15 min. [a] Isolated yield.

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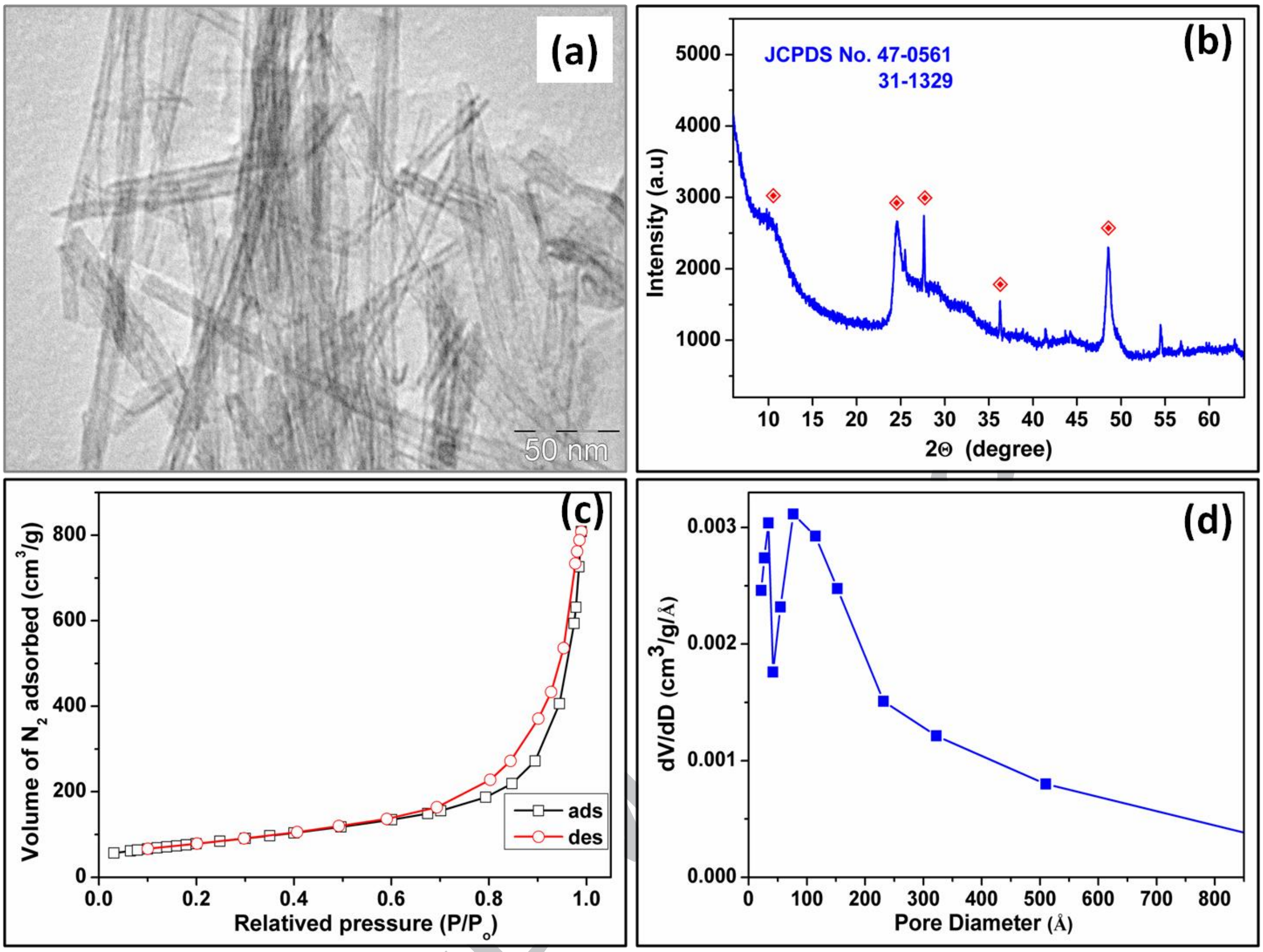

Fig. 4 Characterization of the TNT (a) HR-TEM image, (b) XRD pattern, (c) N_2-adsorption-desorption Isotherm and (d) BJH pore size distributions.

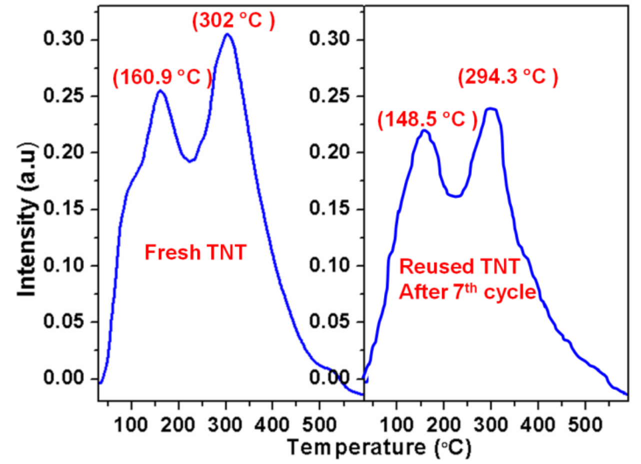

Fig. 3 NH_3-TPD profile of (a) Fresh TNT and (b) Reused TNT after seventh cycle.

2.2. Characterization of TNT

Based on the high catalytic activity of TNT, the physio-chemical properties were analyzed and discussed in detail. The morphology, crystal structure and surface properties are displayed in **Fig. 4**. TEM image reveals (**Fig. 4a**) that random orientation of open tube-like bundles have hollow inner space with openings at both the ends. The cylindrical nanotubes have length > 100 nm with inner and outer diameters of the nanotubes ranging 3-5 nm and 8-12 nm, respectively. In XRD patterns (**Fig. 4b**), the characteristic diffraction peak of TNT exhibited at $2\theta = 10.2^0$ (001) indicates the presence of typical layered crystal structure. All other peaks centred at $2\theta = 24.1$ (202), 28.3 (11-2) and 48.2^0(303) can be well indexed as the monoclinic structure (JCPDS No.47-0561 and 31-1329). In the N_2-adsorption-desorption isotherm (**Fig. 4c**), TNT showed a typical type IV isotherm with a hysteresis loop, confirming the mesoporous nature of TNT.[9] The BET surface area of the sample was calculated to be 286 $m^2.g^{-1}$. The corresponding pore size distribution curve (**Fig. 4d**) by the BJH method consists of two portions with peak values of ca. 2.1-4.2 nm and 4.2-23 nm. Taking into account of the morphology of TNT, the smaller pores relates to the inner hollow spaces of the nanotubes; while the larger pores refers the pores between the nanotubes.[10] The surface area increases from 5.1 $m^2.g^{-1}$ (bulk TiO_2 which used as precursor for the preparation of TNT) to 286 $m^2.g^{-1}$ confirming the tubular structure of TNT.

3. Conclusions

In conclusion, $H_2Ti_3O_7$ nanotubes as a highly efficient catalyst in the synthesis of novel α-aminophosphonates from benzothiazole amines, heteroaldehydes and dialky/diaryl phosphites has been demostrated. This developed green protocol offers several advantages such as requirement of small amount of reusable catalyst, high reaction rates, operational simplicity and mild reaction conditions. The high rate of $H_2Ti_3O_7$ nanotubes is explained by enhanced acidic sites, surface area and mesoporosity.

4. Experimental

4.1. Hydrothermal synthesis of $H_2Ti_3O_7$ nanotubes

As received chemicals were used for catalyst synthesis without further purification. In a typical synthesis process, TiO_2 fine particles (2.5 g) dispersed in 10 M NaOH aqueous solution (200 mL) and transferred to Teflon-lined autoclave (capacity 250 mL) and heated in electric oven at 130 °C/20 h.[11] The white

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precipitate obtained was subjected to washing (twice) with distilled water (800 mL) followed by dil. HCl (0.1 N, 200 mL), finally washed with ethanol (200 mL), and dried at 80 °C for 12 h. The obtained material was denoted as TNT.

*4.2. General procedure for synthesis of α-aminophosphonates **(4a-q)***

Dialkyl/diaryl phosphite (1.0 mmol) was added portion wise over a period of 5 min to the stirred mixture of heterocyclic aldehyde (1.0 mmol) and benzothiazole amine (1.0 mmol) at room temperature. Further 5 mol % of TNT was added to the reaction mixture and the stirring was continued for 15 min. After completion of the reaction as monitored through TLC, the reaction mixture was dissolved in EtOAc (2mL) and the catalyst was separated by centrifugation followed by subsequent washings with EtOAc. The recovered catalyst was reused for the next cycle. The filtrate was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated on a rotary evaporator and the resulting residue was purified by silica gel column chromatography (70:30, hexane/EtOAc) to afford the corresponding pure α-aminophosphonate. The novel α-aminophosphonates were structurally assigned by their IR, NMR (^{1}H, ^{13}C & ^{31}P) and mass spectral (HRMS) analyses.

Acknowledgments

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Supplementary data

General experimental details, characterization data and copies of the NMR (^{1}H, ^{13}C & ^{31}P) spectra of all synthesized compounds and HRMS spectra of **4b**, **4c**, **4j**, **4l** and **4n** is associated with this article can be found, in the online version at

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