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Article

Application of sodium titanate nanotubes doped with vanadium (VNaTNT) as a heterogeneous catalyst for oxidation of sulfides at room temperature

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ABSTRACT

A heterogeneous titanate nanotube (TNT) catalyst containing TiO_2 , Na, and V has been synthesized and used in the chemoselective oxidation of sulfides to the corresponding sulfoxides in the presence of 30% H_2O_2 in water. Some of the advantages of our method include excellent yields, heterogeneous conditions, simplicity, compatibility with a variety of functionalities, and ease of isolation of the products. Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and N_2 adsorption were used for structural and textural characterization of the catalyst (VNaTNT).

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1. Introduction

Sulfoxides and sulfones [1], of which some are important commodity chemicals and pharmaceuticals [2], are most commonly synthesized by the straightforward oxidation of sulfides. This transformation has been carried out by various methods [3–7]. The use of H_2O_2 as the final oxidant offers the advantages that it is a cheap, environmentally benign, and readily available reagent and produces water as the only by-product [8]. It is worth noting that metal catalysts are essential for the production of sulfoxides in high yields and selectivities. There are several reports on some metal-containing catalysts, such as V [9], Ti [10], Cu [11], Ag [12], Fe [13], Bi [14], and W [15] for the oxidation of sulfides to sulfoxides. Unfortunately, most of these reagents are not satisfactory for medium- to large-scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavorable co-products, and high cost.

Among all transition-metal oxides, TiO_2 is the most extensively studied, making it one of the most investigated compounds in materials science. Bulk TiO_2 is known to be a very useful non-toxic, environmentally friendly, corrosion-resistant material, it is frequently used in paint, white pigments, and sunblocks [16]. TiO_2 -based nanotubes have attracted attention because of their potential application as highly efficient photocatalysts [17], in lithium ion batteries [18], in photovoltaic cells [19], and in environmental applications [20]. Sol-gel processing of TiO_2 has been extensively investigated, and modern processes have been developed to refine and control the stability, as well as the phase formation, of the colloidal precursors [21]. Sodium trititanate nanotubes have recently been synthesized using a method proposed by Refs. [22,23], via hydrothermal treatment of the titania precursor with concentrated NaOH aqueous solution (10 mol/L).

Vanadium has been shown to play an important role in oxidation reactions. For example, V-SBA-15, V-MCM-41,

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V-MCM-48, and V-MCF are some interesting V-containing mesoporous silica oxidation catalysts with uniform pore size and high surface area that offer a large concentration of accessible and well-defined active centers, often incorporated into the silica framework [24–29].

In this article, we report on an alcohol impregnation method for the synthesis of ordered sodium trititanate nanotubes (NaTNT) doped with vanadium (VNaTNT) by NaOH and NH_4VO_3 [(4–13) mol%]. The composition and crystallinity of these structures were determined by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption-desorption analysis, and thermal gravimetric (TG) analysis. The catalytic activity of VNaTNT is reported for the oxidation of sulfides with H_2O_2 (Scheme 1).

2. Experimental

Chemicals used were all of reagent grade. Reaction courses and product mixtures were monitored by thin layer and gas chromatographies. A Perkin Elmer Spectrum 65 spectrophotometer was used to obtain infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) from KBr pellets. $\text{Cu K}\alpha$ (0.154056 nm) radiation with automatic control was used to obtain powder XRD patterns on Bruker D8 ADVANCE and PW1830 instruments. Adsorption/desorption of nitrogen at liquid nitrogen temperature was used to determine Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes of the catalysts with a Micromeritics BELSORP mini II instrument. The samples were outgassed at $350\text{ }^\circ\text{C}$ for 12 h under a vacuum of $1 \times 10^{-4}\text{ Pa}$ prior to the adsorption measurements. Catalyst pore sizes were obtained from the peak positions of the distribution curves determined by the adsorption branches of the isotherms. A Joel JEM 2010 scan transmission electron microscope was used to obtain transmission electron micrographs. To perform the TEM measurements, the sample was suspended in ethanol and supported on a carbon coated copper grid. A Shimadzu, MPC-2200 UV-Vis spectrophotometer operating within the range of $190\text{--}900\text{ nm}$ at a resolution of 2.0 nm was used to obtain DRUV spectra.

2.1. Preparation of $\text{V}(x)\text{NaTNT}$

VNaTNT catalysts were prepared by an alcohol impregna-

Scheme 1. Oxidation of sulfides (**1**) to sulfoxides (**2**) and sulfones (**3**) in the presence of VNaTNT catalyst.

tion method. A methanol solution of NH_4VO_3 to achieve a final V content of (4–16) wt% was contacted with the NaTiO_2 support at $60\text{ }^\circ\text{C}$ [22,23], and the methanol was rotary evaporated until complete dryness. The catalysts were then dried overnight in air at $120\text{ }^\circ\text{C}$, followed by calcination at $400\text{ }^\circ\text{C}$ for 4 h, and the catalysts are denoted as $\text{V}(x)\text{NaTNT}$, where the x is the V mass fraction (%).

2.2. Synthesis of sulfoxides and sulfones

H_2O_2 (8 mmol) was added in one portion to a stirred suspension of the selected sulfide (1 mmol) and VNaTNT heterogeneous catalyst in water (5 mL). The resulting slurry was then stirred at room temperature for 30 min. Ethanol (10 mL) was used to filter off and wash the catalyst. Ethyl acetate (5 mL) was added and the resulting solution was dried on anhydrous sodium sulfate and the solvents removed *in vacuo* to afford the crude product. This was then purified by column chromatography using silica gel and 10% EtOAc in hexane as the eluent to afford pure sulfoxide. Sulfones were synthesized by a similar method using 5 mol% of VNaTNT in CH_3CN .

3. Results and discussion

3.1. Physico-chemical characterization

Fig. 1 shows Fourier transform infrared (FT-IR) spectra of the NaTNT, $\text{V}(4)\text{NaTNT}$, and $\text{V}(13)\text{NaTNT}$ samples. The vibrational mode observed at 896 cm^{-1} in the spectrum of the NaTNT reference is assigned to stretching of the Ti–O bonds from a distorted TiO_6 octahedron whose oxygen is unshared [24]. The wavenumber of this vibrational mode increases from 896 in NaTNT to 908 cm^{-1} in $\text{V}(13)\text{NaTNT}$. This confirms incorporation of vanadium into the trititanate structures. Crystalline V_2O_5 is formed in the VNaTNT samples, as implied by the appearance of a typical band of V_2O_5 at ca. $970\text{--}976\text{ cm}^{-1}$. This suggests that the vanadium species are isolated in the VNaTNT samples, or at least highly dispersed on the TNT surface.

Fig. 2 shows XRD patterns of sodium titanate nanotubes NaTNT and VNaTNT. The results indicate that the NaTNT sam-

Fig. 1. FT-IR spectra of NaTNT and $\text{V}(x)\text{NaTNT}$ materials with two different x values. (1) $\text{V}(13)\text{NaTNT}$; (2) $\text{V}(4)\text{NaTNT}$; (3) NaTNT.

Fig. 2. XRD patterns of (1) NaTNT and (2) VNaTNT.

ples studied show good crystallinity and display characteristic peaks at $2\theta = 10.5^\circ$, 24.2° , 28.4° , and 48.2° , commonly associated with monoclinic layered sodium trititanate ($\text{Na}_2\text{Ti}_3\text{O}_7$, JCPDS-ICDD card 31-1329). These correspond to the (001), (201), (111), and (020) crystal planes, respectively.

Fig. 2(2) shows XRD pattern of VNaTNT. The results indicate that the VNaTNT samples show good crystallinity and display the characteristic peaks for $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_5\text{O}_{11}$, and V_2O_5 . The crystalline phases of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_5\text{O}_{11}$ are generally considered characteristic for titanate nanotubular structures [24,25]. The presence of sodium in the interlayer spaces of the trititanate structure is confirmed by the presence of a peak at about $2\theta = 10.5^\circ$ [26].

A number of new sharp reflections are observed along with the signals corresponding to the $\text{Na}_2\text{Ti}_3\text{O}_7$ phase, and this can be ascribed to the presence of different layered sodium titanates ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) with a monoclinic lattice. Conversion of TNTs to larger nanostructures, such as nanoribbons and nanorods [27], is suggested by the appearance of the $\text{Na}_2\text{Ti}_5\text{O}_{11}$. This is in good agreement with the SEM images (Fig. 3).

Fig. 3. SEM images of (a, b) V(4)NaTNT and (c, d) V(13)NaTNT.

Fig. 3 shows the SEM images of V(4)NaTNT and V(13)NaTNT catalysts. V(x)NaTNT exhibits aggregation of regular tube-shaped particles, commonly observed in pure titanate nanotube material [28]. The external diameter size of the nanotubes become smaller and the particles tend to aggregate after increasing the V loading from 4% to 13%, as indicated by the SEM micrographs.

Fig. 4(a) shows the SEM-EDX spectrum of the V(13)NaTNT sample, which shows the presence of V, Na, Ti and O as elements in the V(13)NaTNT structures. According to the energy-dispersive X-ray (EDX) spectrum and its data in Table 1, it can be concluded that a sufficient amount of Na and V was

Fig. 4. (a) EDX-SEM and (b) TEM image of V(13)NaTNT, (c–g) SEM-EDX micrographs and distribution maps of elements in V(13)NaTNT. Particles rich in O (green), Na (orange), Ti (blue), and V (red) are present.

Table 1

Effect of different conditions in the oxidation of diphenyl sulfides to sulfoxides after 0.5 h.

Entry	Catalyst	x/%	H ₂ O ₂ :sulfide	Yield ^a (%)
1	—	—	8:1	3
2	TNT	3	8:1	11
3	V ₂ O ₅	3	8:1	23
4	V ₂ O ₅ /TiO ₂	3	8:1	38
5	NaTNT	3	8:1	27
6	V(4)NaTNT	3	8:1	66
7	V(7)NaTNT	3	8:1	75
8	V(13)NaTNT	3	8:1	87
9	V(15)NaTNT	3	8:1	80
10	V(13)NaTNT	3	8:2	98
11	V(13)NaTNT	4	8:2	85
12	V(13)NaTNT	5	8:2	64

^a Isolated yields.

loaded into the NaTNT. Fig. 4(b) shows TEM images of VNa/TiO₂. The VNaTNT sample was found to include nanotubular structures, either as random groups or aligned bunches. Elemental mapping has been performed for V, Na, Ti, and O, together with SEM imaging, EDX mapping (Fig. 4(c–g)), and EDX linear scanning of VNaTNT (Fig. 5), to check the uniformity of the elemental composition and distribution throughout the VNaTNT samples. The components are heterogeneously distributed throughout the TNT, as shown by EDX maps and linear scans.

Fig. 6 shows the N₂ adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distributions of VNaTNT. A typical type-IV adsorption isotherm with a remarkable hysteresis loop is shown by VNaTNT. This confirms the presence of meso- and macropores. The shape of the N₂

adsorption-desorption isotherms of VNaTNT (Fig. 6(a)), as well as their hysteresis loops, are similar to those previously reported for sodium titanate nanotubes synthesized from low surface area anatase precursors [28–30]. The pore size distribution curves (Fig. 6(b)) show that the sample contains three types of pores. The first type may be ascribed to a smaller portion of mesopores (about 3–5 nm in diameter) attributed to the nanotubes. The second type (about 10–15 nm in diameter) can be ascribed to the parallel assembly of the nanotubes, and the third type (about 35 nm in diameter) may result from randomly assembled nanotubes [23,28,29,31].

The thermal behavior of the NaVTNT is illustrated in Fig. 7(a). TG profile displays two mass loss events, as observed. The initial mass loss of 2.21% was observed at temperatures below 125 °C as a result of the loss of physically absorbed water. The second mass loss of 2.77% was between 230 and 570 °C (mostly at around 430 °C), which can be attributed to the removal of unhydrolyzed isopropoxide ligands bonded in the titanium [32–34]. Approximately 95.02% of the starting mass remained after the second stage. The applicability of the VNaTNT across a wide temperature range is demonstrated by the TGA results.

A DRUV-Vis spectrum of the VNaTNT sample is shown in Fig. 7(b). The spectrum shows one intense absorption band at 247 nm. This band is attributed to charge transfer transitions associated with O²⁻ to V⁵⁺ [35]. Indeed, this band closely resembles that found for NH₄VO₃ [36], indicating an isolated tetrahedral environment of V⁵⁺ in the VNaTNT matrix, which is in good agreement with the literature [37]. On the other hand, the band at 247 nm may also be assigned to a distorted tetrahedral arrangement of V⁵⁺ (as a result of immobilizing/anchoring on

Fig. 5. SEM image and EDX linear scan along VNaTNT (a, b) fresh catalyst, and (c, d) reused catalyst after the sixth run.

Fig. 6. (a) N₂ adsorption-desorption isotherms and (b) pore size distributions calculated by the BJH method of V(13)NaTNT.

Fig. 7. (a) TG curve and (b) DRUV-Vis spectrum of V(13)NaTNT.

the pore windows of the TNT), in a similar manner to that reported for various vanadium-loaded/grafted amorphous/mesoporous silica materials [37,38]. The fundamental absorption edge of TiO₂ appeared in the UV region at about 385 nm [39].

Fig. 8. Solvent effect on the conversion rate and selectivity of diphenyl sulfide oxidation using H₂O₂ catalyzed by V(13)NaTNT.

3.2. Catalytic activity

3.2.1. Oxidation of sulfides to sulfoxides and sulfones

Oxidation was carried out in methanol, *n*-hexane, dichloromethane, acetonitrile, ethanol, acetone, and H₂O to check the feasibility of the VNaTNT system in an organic medium (Fig. 8). Solvents with high hydrogen bonding capacity, such as methanol and water, favor the formation of sulfide with high chemoselectivity [40], as clearly indicated in Table 2 and in

Table 2

Oxidation of sulfides to sulfoxides and sulfones using the V(13)NaTNT/H₂O₂ system.

Sulfide	Yield ^a (%)–Time (h)	
	Sulfoxide 2 ^b	Sulfone 3 ^c
1a	98–0.5	96–1.5
1b	98–0.5	97–1.5
1c	98–1.0	98–2.0
1d	98–1.0	98–1.5
1e	98–1.2	92–2.0
1f	96–1.2	92–2.0
1g	92–1.8	86–3.0

^a Isolated yields.

^b Reaction conditions: Sulfide (2 mmol), H₂O₂ (8 mmol), V(13)NaTNT (3 mol%), H₂O (5 mL), r.t..

^c Reaction conditions: Sulfide (2 mmol), H₂O₂ (15 mmol), V(13)NaTNT (5 mol%), CH₃CN (5 mL), r.t..

Scheme 2. Formation of methylphenyl sulfoxide from the catalyzed oxidation of methylphenyl sulfide and benzaldehyde.

agreement with our studies.

A set of preliminary experiments on diphenyl sulfide were next performed to examine the effects of different amounts of VNaTNT in H₂O at 25 °C (Table 1). No significant oxidation was observed in the absence of VNaTNT in a blank experiment (Table 1, entry 1) and only a low yield of sulfoxide was obtained in the presence of H₂O₂ after 6 h. The optimal ratio of sulfide:H₂O₂:VNaTNT was found to be 2:8:3 for complete conversion of sulfides to sulfoxides. The results are presented in Table 2.

To examine the scope and limitations of this procedure, several functionalized sulfides were selected (Table 2). Dialkyl (**1a**), aryl alkyl (**1b**), and diaryl (**1c**) sulfides could be oxidized to the corresponding sulfoxides in excellent yields. Sulfides with electron-withdrawing (**1d**, **1e**) or donating (**1f**) substituents gave the corresponding sulfoxides in excellent yields with high purity. Importantly, this method is compatible with functional groups, such as esters (**1g**). Oxidations could typically be halted at the sulfoxide stage without over-oxidation to the sulfone.

It is evident that the H₂O₂/VNaTNT system allows these transformations to proceed with excellent selectivity, high yield, and under mild conditions. Furthermore, the use of H₂O₂/VNaTNT makes this method simple, inexpensive, convenient, and practical. Additionally, a competitive H₂O₂/VNaTNT catalyzed oxidation reaction of equimolar amounts of methylphenyl sulfide and benzaldehyde at room temperature leads to the selective formation of methylphenyl sulfoxide in high yield, whereas benzaldehyde remains unchanged (Scheme 2).

The chemoselective oxidation of sulfides to sulfones was also investigated to further demonstrate the efficiency and applicability of the H₂O₂/VNaTNT system. The optimal conditions for the reaction, specified in Table 3, were found using CH₃CN solvent at ambient temperature (sulfide:H₂O₂:VNaTNT = 2:15:5). Application of a smaller amount of oxidizing agent gave a mixture of sulfoxide and sulfone. It was found that a wide variety of diaryl, dialkyl, and arylalkyl sulfides have been oxidized to their corresponding sulfones in excellent yields in CH₃CN at room temperature, as shown in Table 2. Based on a variety of studies, a mechanism, depicted in Scheme 3, has been proposed [3]. The catalytic cycle involves, as a fundamental

Scheme 3. Simplified catalytic mechanism for the oxidation of sulfides in the presence of H₂O₂/VNaTNT system.

step, the formation in the active site of a peroxovanadium species (IV) [5], which is a much stronger oxidant than H₂O₂ [3,5].

The recovery and reusability of the catalyst have been studied. It was observed that the catalyst can be easily recovered quantitatively by simple filtration after the addition of CHCl₃ to the reaction mixture. The wet catalyst was recycled and characterized by neutron activation analysis (NAA), XRD, and FT-IR spectroscopy. The reusability test was carried out under optimized reaction conditions. When the solid catalyst was used for 1, 2, 3, 4, and 5 cycles, the conversion was 98%, 98%, 96%, 94%, and 90%, respectively. Therefore, it is possible to reuse the catalyst without significant loss in its activity. Furthermore, no remarkable differences in the morphology of the fresh catalyst and the spent one could be observed. This may be further evidence for the stability of the catalyst. When the reaction was carried out in MeOH, after six runs the vanadium was leached from the support, as proven by SEM and EDX linear scanning along the VNaTNT (Fig. 4(c) and 4(d)), and by NAA and inductively coupled plasma optical emission spectrometry (ICP-OES) results (V removed is 0.87 wt %, with deviation in the range of ±0.12). This led to deactivation of the heterogeneous catalyst.

To show the merit of the present work in comparison with recently reported protocols [44], we compared the results with respect to the amounts of catalyst used, reaction time, and yields of the products (Table 3). Comparison of VNaTNT with these catalysts, for selective oxidation of sulfides to sulfoxides, shows that the activity of VNaTNT seems to be higher than or equal to other known catalysts (Table 3).

Table 3

Comparison of VNaTNT with other catalysts for the oxidation of PhSMe.

Entry	Reagent	Condition	Time (min)	Yield ^a (%)	Ref.
1	Oxidovanadium(V) complexes/H ₂ O ₂	CH ₂ Cl ₂ /MeOH, r.t.	30	88	[41]
2	Oxido-bridged dinuclear vanadium(V) Schiff base complexes/H ₂ O ₂	CH ₂ Cl ₂ /MeOH, r.t.	30	88	[42]
3	vanadium(V) complexes with tridentate Schiff base ligands/H ₂ O ₂	CH ₂ Cl ₂ /MeOH, r.t.	30	84	[43]
4	V@Cr-MIL(101)	EtOH, r.t.	60	98	[44]
5	VNaTNT/H ₂ O ₂	H ₂ O, r.t.	30	98	this work

^aYield refers to the corresponding sulfoxide.

Graphical Abstract

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Application of sodium titanate nanotubes doped with vanadium (VNaTNT) as a heterogeneous catalyst for oxidation of sulfides at room temperature

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Sodium titanate nanotube doped with vanadium (VNaTNT) has been synthesized, and it showed excellent catalytic performance for the chemoselective oxidation of sulfides in the presence of 30% H_2O_2 in water. FT-IR, XRD, SEM-EDX, TEM, TG, BET and DRUV were used for characterization of the VNaTNT.

4. Conclusions

Sodium titanate nanotubes doped with vanadium (VNaTNT) were synthesized by the hydrothermal treatment of a titania nanotube precursor using an alkali solution (10 mol/L) containing both NaOH and alcoholic NH_4VO_3 . Vanadium was found to play an important role in the oxidation reactions; therefore, vanadium was added to the sodium titanate nanotubes to improve the catalytic performance. VNaTNT is an excellent heterogeneous system for promoting the highly chemoselective and rapid oxidation of functionalized sulfides with H_2O_2 at room temperature in H_2O . It is noteworthy that the reaction tolerates oxidatively sensitive functional groups and the sulfur atom is selectively oxidized.

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钒掺杂的钛酸钠纳米管作为多相催化剂用于室温下硫化物的氧化

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摘要: 合成了一种含有TiO₂, Na和V的多相纳米管催化剂, 采用红外光谱、X射线衍射、扫描电镜、透射电镜和N₂吸附-脱附法对该催化剂的结构和组织性质进行了表征, 并用于水中30% H₂O₂选择性氧化硫化物制备对应的亚砷。该法具有产率极高、多相体系和简便等优点, 可用于含一系列官能团底物的氧化, 产物分离简便。

关键词: 硫化物; 亚砷; 砷类; 负载型钒催化剂; 纳米管

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