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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].

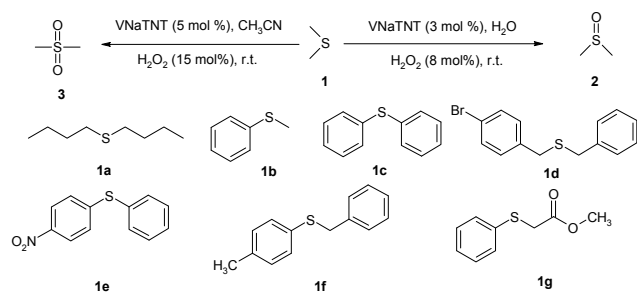
In this article, we report on an alcohol impregnation method for the synthesis of ordered sodium trititanate nanotubes (NaTNT) doped with vanadium (VNaTNT) by NaOH and NH_4VO_3 ((4–13) mol%). The composition and crystallinity of these structures were determined by powder X-ray diffraction (XRD), scanning 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 V(x)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 V(x)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, V(4)NaTNT, and V(13)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 V(13)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-

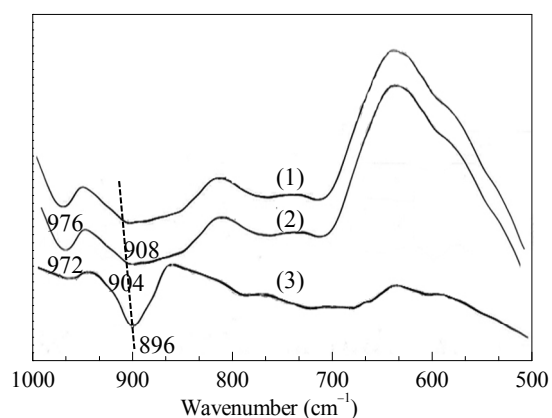


Fig. 1. FT-IR spectra of NaTNT and V(x)NaTNT materials with two different x values. (1) V(13)NaTNT; (2) V(4)NaTNT; (3) NaTNT.

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