



Synthesis and catalytic oxidation property of titanium-zirconium mixed oxide microsphere as well as titanium oxide microcube



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ABSTRACT

Titanium-zirconium mixed oxide microspheres and titanium oxide microcubes have been prepared by using sol-gel processes, which are further modified by chiral sulfonyl chloride in order to improve their activities for oxidation of alkenes. Characterizations reveal that the titanium-zirconium microspheres are solid, but substitution of zirconium with L-(+)-sodium tartrate produces microcubes featuring titanium oxide, which has a hollow structure. In catalysis, both microspheres and microcubes show satisfactory conversions of alkenes, as well as promising outputs of high-valued oxidized products. The linkage of chiral sulfonyl chloride looks efficient for improving catalysis. There is a kind of synergy between metal oxide and attached ligand, which plays a key role in catalytic outputs. Lastly, hydrogen peroxide appears to be a promising oxidant for transformation of aliphatic alkenes. This work puts forward micron-sized titanium materials with interesting structures, which also exhibit satisfactory activity for oxidation of alkenes.

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1. Introduction

The development of efficient and harmless manufactures has become a very attractive target for both academic and industrial areas [1]. Nowadays, these ideas could be addressed by using nanosized catalysts, whose compositions, sizes, morphologies, or aggregations may be modulated by using different preparations, eventually leading to enhanced performances [2]. In this field, significant progress has been made, including magnetic graphene-supported alloys for reduction of nitrophenol [3], cubic Pd nanoparticles for hydrogenation of alkynes [4], or Pt nanowires for oxidation of olefins [5]. Overall, these nanocatalysts are powerful, because they not only bring about satisfactory outputs, but also show minimum wastes, atomic efficiency, and improved recycling as well [6]. However, renewed endeavors deserve to be conducted in the delicate design of catalytic materials, expansion of the reaction scope, and promotion of catalytic outputs as well, which all mean a lot to sustainable development.

Owing to its many properties like high refractive index, ultraviolet (UV) light absorption and semiconductor electronic character, titanium dioxide has been employed as a white pigment, photovoltaic cell or photocatalyst for a long time [7,8]. Moreover, titanium dioxide also appears as a highly potential material for pharmaceutical delivery [9] or other medical applications [10]. Currently, titanium dioxide is being applied for some new areas such as photoelectrochemical sensors [11] and

catalytic production of hydrogen [12], which would obviously contribute to the low carbon economy.

In the meantime, synthesis of titanium dioxide and composites arouses interests for enhanced or new applications. For example, zirconium has been doped into titanium dioxide in order to modulate porosity for pharmaceutical delivery [13]. Furthermore, hollow spheres are prepared by using the sacrificial-template method, showing potentials for photocatalysis [14]. Nevertheless, there is still a big room for exploring new synthetic methods.

Chirality can be observed in biological substances such as DNA and cellulose, but synthesis of micro- or nanosized materials featuring large-scale chiral elements like pores or helices looks difficult [15]. Presumably, chiral templates may agglomerate into micelles in sol-gel, which are further arranged into ordered asymmetric morphology [16]. In practice, use of chiral titanium dioxide may bring about enhanced reactivity for a photoelectrochemical cell [17]. Moreover, chiral induction of such titanium dioxide is also expected. Therefore, how to prepare chiral titanium dioxide is becoming an attractive topic.

The oxidation of alkenes produces many valuable products by using oil resources, showing values for pharmaceuticals, food additives, agrochemicals and polymers [18]. In view of reaction rate and scale, operational safety, as well as production cost, design of efficient catalysts has become a popular choice. Titanium dioxide is nontoxic and inexpensive, and could be obtained from mineral or industrial waste, showing prospects for large-scale uses.

This study aims to prepare titanium oxide with a new texture by doping of either zirconium or L-(+)-sodium tartrate in sol-gel, in order for the oxidation of alkenes. Zirconium has a different diffusion

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rate than titanium in gelation according to the Kirkendall effect [19], which might bring about various textures. Alternatively, L-sodium tartrate is added as a chiral co-template to facilitate texture. The oxalic acid is employed for chelating metal ions. The products are further functionalized by sulfonyl chloride to modulate catalytic centers. This work would contribute to the progress of titanium materials and corresponding catalysis.

2. Experimental

2.1. Materials

Titanium(IV) *n*-butoxide (99%), zirconium(IV) propoxide (70% in 1-propanol), oxalic acid (anhydrous, 98%), L-(+)-sodium tartrate dihydrate (99%), D-(+)-10-camphorsulfonyl chloride (D-CSC, 97%, Scheme 1), L-(-)-10-camphorsulfonyl chloride (L-CSC, 98%, Scheme 1), iodobenzene diacetate (PhI(OAc)₂), *tert*-butyl hydroperoxide (*t*-BuOOH, 70% aqueous solution), hydrogen peroxide (aqueous H₂O₂, 30 wt%), styrene, α -methylstyrene, *R*-(+)-limonene and (-)- α -pinene are purchased from Aldrich, Adamas and Accela. Iodosylbenzene (PhIO) is prepared according to the established procedure [20]. Solvents of HPLC grade and chromatography silica gel are provided by local suppliers.

2.2. Instruments

Scanning electron microscopy (SEM) is performed on JEOL JSM-6700F at 20.0 kV. Transmission electron microscopy (TEM) is tested on JEOL JEM-200CX at 120 kV. Low-angle ($2\theta = 0.5^\circ$ – 10°) and wide-angle ($2\theta = 10^\circ$ – 80°) X-ray diffraction of powdered samples are collected on Philips X'Pert Pro diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) with an interval of $0.05^\circ \text{ s}^{-1}$. The static contact angle is measured according to the conventional sessile drop method by a charge-coupled device (CCD) camera (Sony XC-ST70CE).

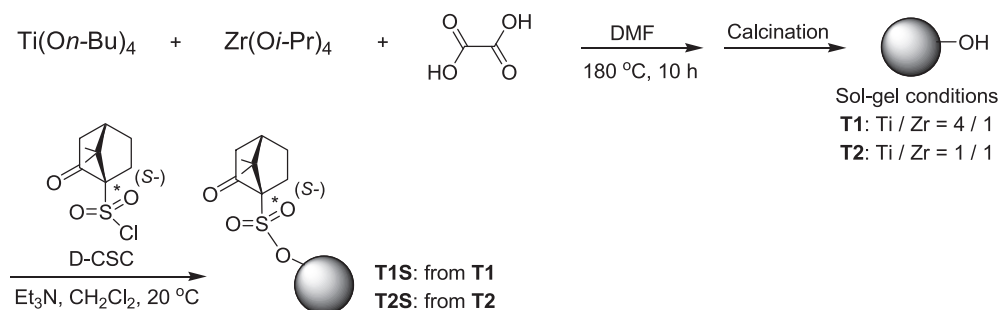
X-ray photoelectron spectroscopy (XPS) is reported on Kratos Axis Ultra DLD, using monochromatic Al K α X-ray (1486.6 eV) as irradiation source, and the binding energy scale is calibrated by using C 1s peak at 284.8 eV. Background subtraction is carried out, and the peaks are fitted by using Gaussian-Lorentz (G/L) product functions with 30% Lorentzian. Thermo-gravimetric analysis (TGA) is performed on NETZSH TG 209C featuring a TASC 414/4 controller under nitrogen protection, with a heating rate of 10 K/min at 308–1073 K. Differential scanning calorimetry (DSC) is carried out on NETZSH DSC 214 under nitrogen protection, with a heating rate of 10 °C/min at 32–300 °C.

BET surface area, pore volume, pore radius and pore size distribution are reported on Micromeritics ASAP 2020, using N₂ adsorption isotherms at 77.35 K. Samples are degassed at 150 °C in vacuum before testing. Surface area is calculated on these isotherms using the multi-point Brunauer-Emmett-Teller (BET) method based on adsorption in P/P_0 of 0.06–0.3. Total pore volume is obtained from N₂ adsorbed at $P/P_0 = 0.97$. Pore volume and pore radius are determined using the Barrett-Joyner-Halenda (BJH) method. FT-IR spectra are tested in KBr pellets on Bruker Tensor 27, with wave numbers of 400–4000 cm⁻¹. Raman spectra are recorded on a Horiba HR 800 spectrometer with a charge-coupled device (CCD) camera detector, and the 514 nm line is derived from a Spectra Physics 2018 Argon/Krypton Ion Laser system.

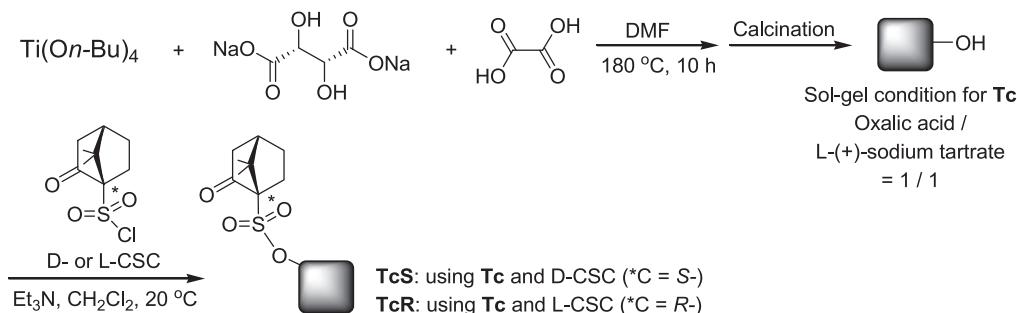
Internal chirality of synthetic samples is determined according to literature [21]. In practice, sample (50 mg) and L- (or D-) valine (20 mg) are added to distilled water (50 mL). The mixture is vigorously stirred at 25 °C for 100 min. Concentration of L- (or D-) valine is measured by using UV spectra at 215 nm (UV 1800, Shimadzu) with sampling at regular intervals. Adsorption percentage is calculated based on the adsorption of 0 min according to Lambert-Beer's Law, and plotted as a function of time.

Thin layer chromatography (TLC) is conducted on glass plates coated with GF₂₅₄ silica gel, whose coloration is performed in phosphomolybdic acid (PMA)/ethanol (5 wt%) under heating. GC-MS is tested on GCMS-QP2010 Plus, Shimadzu, with an Rxi-5ms

1. Synthesis and functionalization of titanium-zirconium mixed oxide microspheres



2. Synthesis and functionalization of titanium oxide microcubes



Scheme 1. Synthesis of catalysts.

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