



Sulfated and phosphated H-type niobate nanotubes as solid acid catalysts



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ABSTRACT

Highly pure sodium niobate nanotubes (NaNbNTs) were prepared by treating nonporous Nb₂O₅ powder with 1.0 M NaOH solution at 423 K. SEM revealed that these NaNbNTs formed nanotube-bundles with diameters of 50–250 nm and lengths of several microns. A TEM image of nanotubes indicated that they had outer diameters of 15–20 nm and inner pore diameters of 3–4 nm. BET surface area and pore volume of NaNbNTs were 65 m² g⁻¹ and 0.17 mL g⁻¹, respectively. Treatment with diluted phosphoric or sulfuric solutions transformed NaNbNTs into phosphate- or sulfate-promoted protonated niobate nanotubes (PO₄⁻³/HNbNTs and SO₄⁻²/HNbNTs), which had a surface area of ~80 m² g⁻¹, a pore volume ~ 0.26 mL g⁻¹ and a surface that was densely covered with acid sites (1.0–1.5 mmol g⁻¹). Owing to the high density of its acid sites, SO₄⁻²/HNbNTs outperformed a superacidic sulfated metal oxide like SO₄⁻²/HfO₂ in catalyzing the formation of cyclic acetals from carbonyl compounds and ethylene glycol. TPD/NH₃ investigations indicated that the acid site density in PO₄⁻³/HNbNTs was even higher than in SO₄⁻²/HNbNTs, but its activity in catalyzing the formation of cyclic acetals was lower. These results reveal that acid sites in PO₄⁻³/HNbNTs had a severe steric effect owing to the thick surface phosphate layer, permitting only the adsorption of small molecules. Large molecules, like heptanal, may not be easily adsorbed on a surface that is densely populated with PO₄⁻³ groups, causing PO₄⁻³/HNbNTs to have a lower activity than SO₄⁻²/HNbNTs, which had a lower surface population of equally bulky SO₄⁻² groups.

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1. Introduction

Liquid acid catalysts or acidic halides such as H₂SO₄ and AlCl₃ are used in many acid-catalyzed reactions, including Friedel–Craft reactions, esterification, hydration and hydrolysis. These conventional acid catalysts are hazardous and corrosive, and are difficult to separate and regenerate. Solid acid catalysts are stable and safe; readily separable from reaction mixtures, and reusable; they pose little environmental hazard and are convenient to use. Therefore, many solid acids such as pillar clay, heteropoly acids, ion-exchange resins, sulfonated carbon materials, sulfated metal oxides and zeolites have been studied [1,2]. Microporous solid acid catalysts, such as zeolite, have a high surface area, but their small pores limit the rate of diffusion of bulky reactants through them and reduce

product yields. Accordingly, large quantities of such catalysts are required when they are used in solid acid catalysis.

One-dimensional mesoporous nanotubes have large interior voids, which confine reactants, improving their catalytic performance; they high surface areas, which provide many active sites where the catalytic reaction can proceed. Additionally, these materials typically have a hierarchical pore structure, comprising spaces in the voids of the hollow tubes and those between the nanotubular particles. This pore structure increases the efficiency of diffusion of the reactants and products and, thereby, the efficiency of the catalyst. Recently, highly pure protonated titanate nanotubes (HTNTs) were prepared by a simple hydrothermal method in a strongly alkaline aqueous solution [3]. These nanotubes exhibited excellent catalytic activity and selectivity in the Friedel–Craft alkylation of toluene with benzylchloride [3] and in the synthesis of renewable diesel and jet fuel range alkanes [4]. These HTNTs exhibited strong Brønsted acidity, and their mesoporous tubular structure favored the catalytic reaction as the reactant molecules were confined within the nanotubes [5].

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Niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) is a strong acidic solid ($H_0 = -5.6$) whose acidity is retained even in the presence of water molecules that is present in many acid-catalyzed reactions [6]. However, it has relatively few acid sites and its surface acidity is greatly reduced by thermal treatment at high temperature (>700 K) which crystallizes the amorphous niobium oxide phase. The treatment of niobic acid with phosphoric acid is effective for maintaining a high surface area after calcination at high temperature [7]. Thus, this treatment enhances the catalytic activity of niobium oxide in some acid-catalyzed reactions, such as the dehydration of cyclohexanol, the alkylation of benzene with methanol and the hydration of ethylene [6–8].

Nb_2O_5 nanotubes have been fabricated by, for example, a two-step solution route, in which Nb_2O_5 nanorods are formed first and then selectively dissolved along the [001] direction to generate Nb_2O_5 nanotubes [9], or by a cathodic electrochemical strategy to form Nb_2O_5 nanotubes that are supported on Nb foil [10]. These methods, however, are tedious. Mallouk et al. reported the spontaneous formation of nanotubes in exfoliated nanosheets of some of particular hexaniobates and Ruddlesden–Popper phases of layered perovskites [11,12]. Several protonated niobate nanosheets, such as HNb_3O_8 , $\text{H}_4\text{Nb}_{16}\text{O}_{17}$, HTiNbO_5 and $\text{HTi}_2\text{NbO}_{17}$, are strong solid acids, whose Brønsted acid sites, like those of niobic acid, are functional in the presence of water molecules [13,14]. Based on the above findings, acidic anion-promoted protonated hexaniobate nanotubes were prepared herein by firstly utilizing Nb_2O_5 powder and the hydrothermal method to prepare NaNbNTs , and then performing a mineral acid treatment on them using diluted H_2SO_4 or H_3PO_4 solution. The acid treatment had two functions; the first was to replace the Na^+ ions in NaNbNTs , which were formed by the hydrothermal treatment of Nb_2O_5 , with H^+ to yield HNbNTs ; the second was to increase the acidity of HNbNTs and their thermal stability against sintering by the adsorption of PO_4^{-3} and SO_4^{-2} anions on their surfaces. Our experimental results indicate that these new solid acids exhibit a hierarchical pore structure, a high acid site density and an interesting steric property related to the molecular size of the reactant.

The importance of high acid site density in solid acid catalysis is being increasingly reported upon. A simple hydrothermal saline-promoted grafting protocol increases ten-fold the acid site density of a mesoporous sulfonic acid SBA-15 silica and three-fold the yield of biodiesel compared with those achieved using traditional grafted materials [15]. A mesoporous niobium phosphate, synthesized using a cetyltrimethylammonium bromide template, is an excellent solid acid for catalyzing the dehydration of fructose to 5-hydroxymethylfurfural in water [16]. Its excellent catalytic activity is attributable to its high acid site density and tolerance to water. A combination of mild acid treatment and aluminum grafting has been proven to increase the acid site density in a natural aluminosilicate (Montanit 300). Its high acid site density and its mesoporous structure have been found to be critical to its high catalytic activity in the de-polymerization of polyethylene to form liquid fuel-grade hydrocarbons and lower olefins [17].

The results in this manuscript will show that the treatment of HNbNTs with phosphoric acid causes a three-fold increase in the acid site density and a four-fold enhancement in its catalytic activity in the formation of cyclic acetal by a reaction of heptanal with ethylene glycol (EG). More interestingly, $\text{SO}_4^{-2}/\text{HNbNTs}$ catalyst, with the same acid strength distribution as $\text{PO}_4^{-3}/\text{HNbNTs}$ but a lower acid site density, was an order of magnitude more active than $\text{PO}_4^{-3}/\text{HNbNTs}$ in acetal formation. We will demonstrate further that the catalytic activity of the $\text{PO}_4^{-3}/\text{HNbNTs}$ catalyst was lower because of a steric effect that arises from the molecular size sieving effect of the surface phosphate layer that was formed by the treatment with phosphoric acid. The catalytic activity of the

sulfated niobate nanotubes even exceeds that of a superacidic sulfated metal oxide such as $\text{SO}_4^{-2}/\text{HfO}_2$. These results shed light on the structure of the acid sites in these anion-promoted HNbNTs and the reaction path to the cyclic acetal product and a bulky hemiacetal by-product.

2. Experimental

2.1. Preparation of catalysts

2.0 g of Nb_2O_5 powder (Strem Chemicals, 99.9%) was mixed with 200 mL of 1.0 M NaOH in a 1.0 L perfluoroalkoxy container. The mixture was maintained at 423 K for seven days. At the end of the reaction, a small quantity of flake-like material was floating on the surface of the reaction mixture. After the flake had been carefully removed using a pipette, the resulting reaction mixture was filtered by vacuum filtration to yield a paste. The paste was thoroughly washed in 1000 mL of deionized water for 1.0 h. This washing process was performed three times. The powder was then filtered and dried at 383 K overnight to yield the sodium niobate nanotubes (NaNbNTs).

To prepare $\text{PO}_4^{-3}/\text{HNbNTs}$ and $\text{SO}_4^{-2}/\text{HNbNTs}$, the wet NaNbNTs paste was treated with a diluted phosphoric acid or a sulfuric acid aqueous solution (0.10–0.50 M). 1.0 g of NaNbNTs was mixed with 500 mL of acid solution in a 1.0 L round-bottom flask. The reaction mixture was stirred for 2.0 h and then filtered. The acid treatment was carried out three times. The filtered paste was dried overnight at 423 K to yield the anion-promoted nanotubes. Wherever necessary, some of the nanotube samples were dried or calcined at 423–1073 K for a specified period. The acid treatment was the same for the preparation of HNbNTs , but with 0.20 M HCl solution. Following HCl treatment, the filtered paste was washed using deionized water, as described above, until no Cl^- ion was detected in the filtrate with AgNO_3 solution. The final paste was again dried overnight at 423 K to yield HNbNTs powder.

2.2. Characterization of catalysts

The BET surface areas of the catalysts were measured using a Micromeritics ASAP 2010 with N_2 gas, at the liquid nitrogen temperature. The distribution of pore sizes in the catalysts was determined using the BJH method. X-ray powder diffraction patterns were obtained using a Shimadzu Lab-X XRD-6000 diffractometer with $\text{Fe K}\alpha$ irradiation ($\lambda = 1.93604$ Å). A JEOL JSM-6700F field-emission scanning electron microscope was used to observe the morphology of the catalyst at various calcination temperatures. A Phillips CM-200 transmission electron microscope, coupled with an EDX detector (energy-dispersive X-ray), was used at an accelerating voltage of 200 kV to observe the fine structures of the catalysts and to analyze their elemental compositions. The Na^+ contents of the catalysts were obtained by ICP-AES using a Jarrell-Ash ICAP-9000. The catalysts were digested using concentrated HF and standard solutions of known concentrations were used as calibration standards.

XPS spectra were obtained using a VG Scientific ESCALAB 250 X-ray photoelectron spectrometer with an Al anode; the vacuum in the analysis chamber was at a pressure of less than 5.0×10^{-8} torr. The C (1s) XPS signal at 284.5 eV from the residual carbon in the catalyst was used as the calibration standard for the binding energy (BE) of the observed signals in the XPS spectra.

The temperature-programmed desorption of ammonia (TPD/ NH_3) for evaluating the acidity of the catalysts were conducted using a Micromeritics Autochem 2910 with both a TCD and an on-line quadrupole mass spectrometer (Prolab, Thermo Onix) as

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