



## Protonated titanate nanotubes as solid acid catalyst for aldol condensation



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### ABSTRACT

One-dimensional protonated titanate nanostructures were tested as solid acid catalysts in the condensation reaction between benzaldehyde and cyclohexanone. Two morphologies were employed – nanotubes and nanoribbons. *In situ* diffuse reflectance infrared Fourier transform spectroscopy of adsorbed NH<sub>3</sub> and NH<sub>3</sub> temperature programmed desorption revealed that both protonated titanate nanotubes and nanoribbons possess Lewis and Brønsted acid sites with medium acid strength, whereas only nanotubes have also strong acid sites. Therefore only protonated titanate nanotubes revealed an efficient catalyst that was also successfully applied to other reaction systems with substituted benzaldehyde derivatives. Recycling studies showed no significant decrease in the catalytic activity of protonated titanate nanotubes in five cycles and even showed an excellent performance in the large scale experiment. In addition, protonated titanate nanotubes did not require any activation prior to the reaction. The mechanism is proposed to describe the condensation process over the catalyst.

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### 1. Introduction

Aldol condensation is one of the most important organic reactions for coupling of carbonyl compounds and formation of a new C–C bond, which can be catalyzed with either acids or bases [1]. The characteristic products,  $\alpha,\beta$ -unsaturated carbonyls, represent important building blocks in organic synthesis due to their activation towards nucleophiles for 1,2 and 1,4-additions. They are reported to be potentially bioactive [2] and are produced during biomass conversion, especially in a biofuel production [3]. In the industry,  $\alpha,\beta$ -unsaturated carbonyls are widely applied as final or intermediate molecules in perfume industry [4,5]. On the other hand, coupling of substituted benzaldehydes with cycloalkanones leads to the formation of  $\alpha,\alpha'$ -bis(substituted)benzylidene cycloalkanones. These compounds are common precursors for the synthesis of agrochemicals and pharmaceuticals, especially bioactive pyrimidine compounds and a HIV-1 integrase inhibitor [6,7], but the current synthesis methods do not enable high product yields.

Despite wide applicability of aldol condensation, it has several industrial drawbacks in regard to the environment. In the industry, the aldol condensation is catalyzed with a stoichiometric amount of aqueous base, thus leaving behind large quantities of waste salts that need to be disposed of [8]. Homogeneous catalysts are often corrosive, difficult to handle and cannot be recycled. Another and rather important disadvantage is poor reaction selectivity of aldol condensation. As an alternative to the above mentioned limitations, heterogeneous catalysis has emerged, where solid catalysts are normally non-corrosive and the handling of the reaction mixture is facilitated [9].

One dimensional (1D) protonated titanate nanostructures have been proposed as potential solid acid catalysts [10–12]. They can be prepared in large quantities by conversion from 1D sodium titanates with an ion exchange process. In addition, sodium titanates can be synthesized in two distinct morphologies, *i.e.* nanotubes and nanoribbons [13]. Nanotubes are scrolls of one or few titanate layers, whereas nanoribbons are much larger and thicker parallel-leveled structures composed of numerous stacked titanate layers [14].

Kitano et al. first reported about the application of protonated titanate nanotubes (HTiNTs) as solid acid catalysts [10]. HTiNTs catalyzed Friedel-Crafts alkylation of toluene with benzyl chloride,

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and the product was obtained with a 90% yield after 3 h of the reaction performed at room temperature [10]. Since then, the correlation between the structural properties of the material and its catalytic activity has been intensively studied [15,16]. The acidity of protonated titanates arises from surface coordinatively unsaturated  $\text{Ti}^{4+}$  centres and surface hydroxyl ( $-\text{OH}$ ) groups. The former are attributed to Lewis acid sites when Brønsted acid sites represent surface  $-\text{OH}$  groups, which can be either in a terminal or in a bridging mode [15]. Density functional theory (DFT) calculations have confirmed that the bridging  $-\text{OH}$  groups have higher acid strength than the terminal ones [15]. Hydroxyl groups are present also in the interlayer space between the titanate layers but they do not participate in the catalytic reaction [16]. The strength of Brønsted acid sites depends also on morphology. Protonated titanate nanotubes have higher Brønsted acidity than nanosheets because of lattice distortion of scrolled titanate layers [10,15].

Despite the low-cost production that provides large quantities of 1D protonated titanates, there are few reports about their application as solid acid catalysts. Exfoliated protonated titanate nanosheets have been proven as more efficient solid acid catalysts than bulky protonated titanates for the dehydration of D-xylose into furfural [11]. Protonated titanate nanosheets have a larger specific surface area and therefore a larger amount of accessible active catalytic sites. Furfural yield was approximately 40% when the reaction was carried out at 160 °C in a water-toluene solvent system in a microreactor [11]. Protonated titanate nanotubes were also reported to excel over the catalytic performance of conventional solid acid catalysts such as sulphated zirconia, sulphated alumina, and different zeolites (H-ZSM-5, H-MOR and H- $\beta$ ). This was shown on the hydroxyalkylation/alkylation of 2-methylfuran with *n*-butanol from lignocellulose to synthesize diesel precursors [12].

In the present work we tested 1D titanate nanostructures as solid catalysts for aldol condensation between benzaldehyde and cyclohexanone. 1D protonated titanates were characterized with various analytical techniques in order to correlate materials' morphological and surface properties with their catalytic activity. The surface properties of 1D protonated titanates governed the optimal reaction conditions at which the condensation reaction proceeded with the highest conversion and yield. The generality of the best performed catalyst was evaluated also from the condensation reaction between different substrates. Repetition cycles and a large scale experiment were conducted in order to test the catalyst's potential for industrial application. The mechanism of the reaction is also proposed.

## 2. Experimental section

### 2.1. Material synthesis

Catalyst materials (protonated titanate nanotubes and nanoribbons) were synthesized according to the method already reported elsewhere [13,17]. In short, a suspension of  $\text{TiO}_2$  and 10 M NaOH (1 g  $\text{TiO}_2$ /10 mL 10 M NaOH) was stirred at room temperature for 1 h and ultrasonicated for 30 min. The suspension was transferred to a Teflon-lined autoclave, and the filling volume was 80%. The reaction mixture was hydrothermally treated for three days at 135 and 175 °C to obtain sodium titanate nanotubes (NaTiNTs) and nanoribbons (NaTiNRs), respectively. The resulting materials were washed twice with deionized water, once with ethanol, and dried overnight at 100 °C. Protonated titanate nanotubes (HTiNTs) and nanoribbons (HTiNRs) were prepared from the parent sodium titanate with an ion exchange process. NaTiNTs and NaTiNRs were washed several times with 0.1 M  $\text{CH}_3\text{COOH}$  and rinsed with deion-

ized water till the pH of the supernatant was 5.5 [17]. The products were washed with EtOH afterwards and dried overnight at 100 °C.

### 2.2. Material characterization

The morphology of HTiNTs and HTiNRs was investigated with scanning (FE-SEM, Jeol 7600F) and transmission electron microscopes (TEM Jeol 2100, 200 keV). Samples for SEM characterization were prepared as a water dispersion of the material, where one drop was placed on a polished Al sample holder. The holder with the products was coated with a 3 nm thick carbon layer prior to the SEM investigation. For TEM analyses, the sample was dispersed in methanol and ultrasonicated for 20 min. One drop of the dispersion was then deposited on a lacy carbon film supported by a copper grid.

The sodium content of the materials was analyzed with the FE-SEM equipped with an energy-dispersive X-ray spectrometer (EDXS) elemental analysis system. The materials were pressed into pellets and placed on a carbon tape on an Al sample holder. The holder with the samples was coated with a thin carbon layer prior to the EDXS analyses.

The phase composition of the samples was determined with X-ray powder diffraction (XRD), using a D4 Endeavor, Bruker AXS diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and a Sol-X energy-dispersive detector. Diffractograms were measured in the  $2\theta$  angular range between 5 and 60° with the step size of 0.02 °/s and the collection time of 3 s.

Nitrogen adsorption measurements were executed with a Micrometrics ASAP 2020 analyser. Specific surface areas of HTiNTs and HTiNRs were determined with a Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) calculation was used to determine their pore size distribution. The samples were outgassed overnight at 100 °C prior the analyses, which were then performed at  $-196 \text{ °C}$ .

$\text{NH}_3$  thermal programmed desorption (TPD) measurements were carried out using the AutoChem II 2920 station. The samples (30–50 mg) were placed in a U-shaped quartz reactor with an inner diameter of 0.5 cm, which was first pre-treated under He (Purity 5.0, from Linde) at 150 °C for 2 h, and exposed to a flow of 10%  $\text{NH}_3$  in helium (from SIAD) for 1 h afterwards. The sample was then purged with a flow of He ( $50 \text{ mL min}^{-1}$ ) for 20 min at 25 °C in order to remove the weakly adsorbed species. TPD was executed with a heating rate of  $5 \text{ °C min}^{-1}$  till 700 °C. The desorbed products were analyzed with a thermal conductivity detector. The amount of desorbed  $\text{NH}_3$ , expressed as mmoles of  $\text{NH}_3$  per grams of catalyst, was determined using a calibration curve.

*In situ* diffuse reflectance infrared Fourier transform (DRIFT) analysis was performed using a Thermo Electron Nicolet 4700 Fourier transform infrared spectrometer with a Smart Accessory for diffuse reflectance measurements and an *in situ* cell. The DRIFT spectra were scanned in the region of  $4000\text{--}400 \text{ cm}^{-1}$  at the resolution of  $4 \text{ cm}^{-1}$ . The final spectra correspond to an accumulation of 200 scans. A gold mirror was used for reference measurements. The surface of the sample was cleaned by heating the cell at 100 °C under vacuum. Then, the sample was cooled to room temperature and the probe molecule was chemisorbed by passing a flow of 1 vol.% of  $\text{NH}_3$  in He for 30 min. The non-bonded and physisorbed  $\text{NH}_3$  was evacuated under the flow of nitrogen for another 60 min afterwards. Desorption started with heating the cell at a rate of  $10 \text{ °C min}^{-1}$  under the same atmosphere and the spectra were collected every 50 °C.

Raman spectra were recorded at room temperature with a WITec Alpha 300 scanning confocal microscope using a 633 nm laser. The power of the laser beam was set to 4 mW in order to avoid any sample damage and the spectral resolution was  $3\text{--}4 \text{ cm}^{-1}$ . For the analysis, the samples were manually pressed onto

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