



Oxidative Dehydrogenation of Propane Over Vanadia Supported on Nanostructured Titania

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Abstract

Vanadia catalyst supported on nanostructured titania was synthesized by incipient wetness impregnation method and utilized for propane oxidative dehydrogenation (ODH). Pristine titanate nanotube possessing BET surface area of $400 \text{ m}^2 \text{ g}^{-1}$ was synthesized by a facile hydrothermal method using TiO_2 P25 as a precursor. XRD and Raman analysis confirmed formation of the layered titanate phase. The XRD patterns of vanadia impregnated catalyst demonstrated the development of anatase phase without appearing rutile. TPR and XRD analysis showed high dispersion of vanadia on nanostructured titania. Activity tests showed elevation of propylene yield and conversion as a function of temperature. Selectivity decreased at low reaction temperatures and increased at higher temperatures.

Keywords: Propane, Oxidative dehydrogenation, Vanadia catalyst, Titanate nanotube.

Introduction

Propylene which is one of the most important building blocks in different petrochemical and polymer processes, mostly obtained by high energy consumer steam cracking at high temperatures. Accelerating propylene demand give an impetus to development of alternative processes with lower energy consumption. Oxidative dehydrogenation (ODH) of propane is amongst proposed potential solutions to this demand growth which in contrast to nonoxidative pathways, presents no thermodynamic limitations and is a highly exothermic reaction [1]. Generally, Bulky vanadium pentoxide demonstrates a relatively low catalytic performance in selective alkane oxidation. In other hand supporting on oxides such as titania leads to development of catalysts with superior activity and selectivity. Catalytic performance of vanadia catalysts depends on the specific support, promoters, vanadia loading, calcination temperature [2]. Conventional anatase titania suffers from low surface area [3]. Since the innovative work of Kasuga [4], TiO_2 and/or titanate nanotubes possessing large specific surface area and specific structure have appeared to be a promising and notable material. High-yield nanotubes could be effectively prepared by using a simple hydrothermal treatment of a TiO_2 source. The process is cost-effective, simple, and environmentally friendly. In This contribution, vanadia catalyst supported on titania nanotube was investigated for the first time in propane oxidative dehydrogenation. Propylene yield and selectivity as well as propane conversion were acquired as a function of reaction temperatures.



Experimental

Typically, 1.7 g of Degussa TiO₂ P25 was added to 150 mL of 10 M aqueous solution of NaOH. The resulting mixture was stirred for 30 min, and transferred into a Teflon-lined stainless steel autoclave. The sample maintained at 140°C for 24h. After centrifugation and the sample was washed with 0.1 M HNO₃ aqueous solution. The acid-treated sample was oven-dried at 110°C overnight.

The incipient wetness impregnation method utilized in the preparation of the catalyst (VTNT-5). VTNT-5 catalyst was prepared by supporting 5 wt% vanadia on titanate nanotubes. A measured amount of ammonium metavanadate and oxalic acid (molar ratio=1/2) was added to calculated volume of deionized water correspond to the total pore volume of the support. Once oven-dried at 110°C overnight, the powder was calcined in static air at 500°C.

Oxidative dehydrogenations of propane (ODHP) experiments were carried out in a fixed-bed down-flow reactor with inner-diameter of 6 mm at atmospheric pressure. About 160 mg of the catalyst with a mesh size of 60 to 100 was loaded into the reactor. The catalyst was pretreated in 20 cc/min flow of dry air at 300°C before each run. After cooling down to 200°C a flow of air (99.995%) and propane (99.8%) conducted through the catalyst bed with propane/O₂ ratio equal to 2 and a total gas flow rate of 20 cc/min. The temperature was increased by steps of 50°C up to 500°C. Analysis of the composition of the reactor effluent was carried out on-line using a Varian CP-3800 gas chromatograph equipped with FID and TCD.

Results and Discussion

XRD was used to investigate the phase structure of the nanotubes. Figure 1a demonstrates the XRD patterns of uncalcined acid-treated titanate nanotube. The diffraction peaks can be assigned to H₂Ti₂O₅·H₂O (JCPDS: 47-0124) which is totally different with XRD patterns of P25 (Not shown). As EDX analysis (Not Shown) evidently demonstrated the absence of sodium ions in the acid-treated nanotubes, the obtained nanotubes can be attributed to the hydrogen titanates. The diffraction peak around 10° corresponds to the interlayer spacing between the titanate sheets [5].

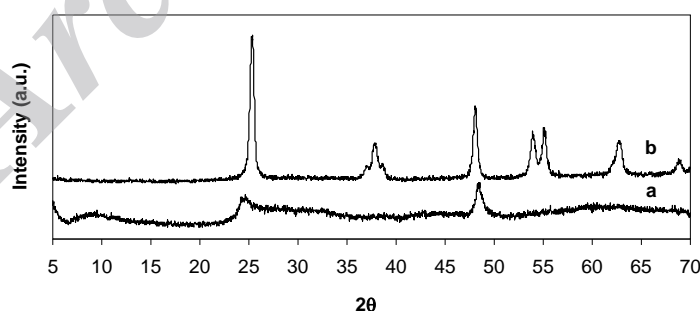


Figure 1. XRD pattern of (a) titanate nanotube and (b) VTNT-5.

The BET specific surface area obtained for TiO₂ P25 and titanate nanotubes being 48 and 404 m² g⁻¹, respectively. Formation of high surface area nanotubes from a typically low surface area TiO₂ precursor causes a significant increase on the surface area of the material.

The Raman spectra of acid-treated titanate nanotubes is shown in Fig. 2. The band at 448 cm⁻¹ assigned to Ti-O-Ti vibration. The band at 825 cm⁻¹ can be related to covalent Ti-O-H bond [6].

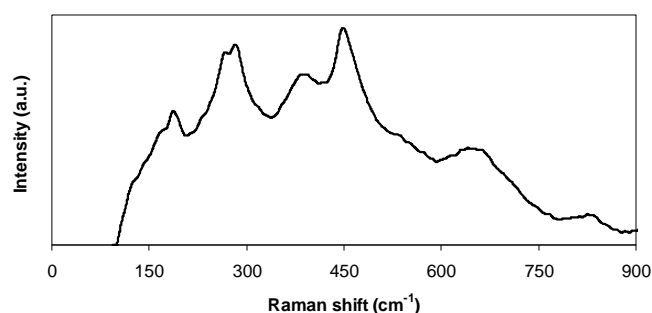


Figure 2. Raman spectra of titanate nanotube.

Powder XRD patterns of the vanadia containing catalyst is shown in Fig. 1b. As can be noted from this figure, the corresponding patterns of VTNT-5 revealed solely the presence of crystalline phase of the relevant support. The absence of V_2O_5 diffraction lines is a consequence of very fine dispersion of vanadia species on the support. The phase change from hydrogen titanate to anatase is evidenced by the XRD patterns [7]. Emerging no rutile phase hints that at relatively high calcination temperature applied for VTNT-5, anatase to rutile transformation (ART) did not occurred. ART is claimed to lower V/Ti catalytic systems activity in propane ODH. BET surface area of VTNT-5 is $72.6 \text{ m}^2 \text{ g}^{-1}$ which demonstrates sintering of the pristine titanate nanotube structure as a result of calcination and presence of vanadia.

Temperature programmed reduction (TPR) with hydrogen is depicted in Fig. 3. The H/V ratio close to 2 indicates that vanadia phase may reduced to V_2O_3 . The degree of reduction for bulk vanadium pentoxide is very low at temperatures below 750°C , while vanadia supported on nanostructured titania demonstrated a reduction maximum peak at around 500°C . This temperature is ascribed to the presence of monomeric vanadia species on the titania surface [1, 7].

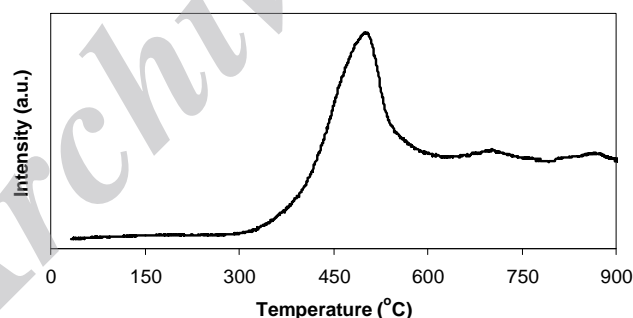


Figure 3. H_2 -TPR profile of VTNT-5.

Figure 4 shows the conversion of propane and propylene yield as well as propylene selectivity as a function of reaction temperatures. Propylene, CO, CO_2 , and H_2O were main products of the ODH of propane. The conversion of propane and propylene yield increased when the temperature increased. At low temperatures selectivity decreased as a result of consecutive combustion of produced propylene and CO_x production. By elevation of the temperature, oxygen consumption increased and the conversion varied little and the selectivity to propylene increased as formation of propylene requires the least amount of oxygen [3].

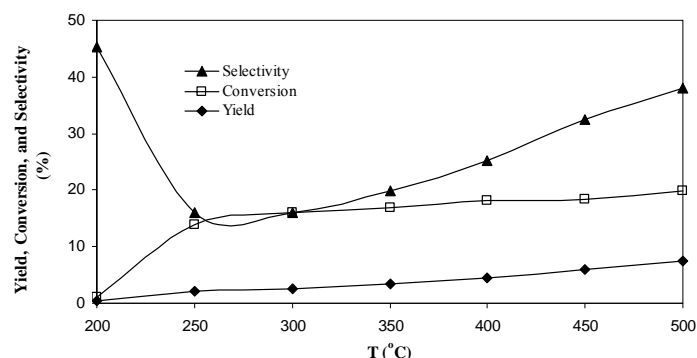


Figure 4. Yield, conversion, and selectivity vs. temperature in propane ODH on V/Ti catalytic system.

Conclusions

Highly dispersed monomeric vanadia species supported on nanostructured titania are synthesized and utilized in oxidative dehydrogenation of propane at different reaction temperatures. Vanadia deposition leads to a support phase change from hydrogen titanate to anatase phase without formation of rutile. The BET specific surface area of the resulted catalyst is higher than TiO₂ P25 precursor. Propylene yield as well as propane conversion raises with temperature increment. Selectivity change is quite different as the oxygen concentration varies along the catalyst bed. Propylene yield is about 7.5% at reaction temperature of 500 °C.

Acknowledgements

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