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Stability and catalytic performance of vanadia supported on nanostructured titania catalyst in oxidative dehydrogenation of propane

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ABSTRACT

Titanate nanotubes with a high specific surface area were synthesized by the simple hydrothermal method and investigated as support for V_2O_5 catalyst in oxidative dehydrogenation of propane (ODP). The structures of pristine nanotubes as well as the prepared catalysts were investigated by XRD, Raman, FTIR, HRTEM, SEM, EDS, BET, and XPS techniques. The characterization of the as-synthesized nanotubes showed the synthesis of hydrogen titanate nanotube. The incipient wetness impregnation method was utilized to prepare VTNT-x (x = 5, 10, and 15 wt.% vanadia supported on nanotube) together with VTi5 (5 wt.% vanadia supported on Degussa P25). The anatase phase was developed in VTNT-x catalysts upon calcination along with specific surface area loss. Higher vanadia loading resulted in the lowering of support capacity in maintaining vanadia in dispersed state such that eventually crystalline vanadia appeared. The measured catalyst activity demonstrates that in spite of major support surface area loss in VTNT-5 catalyst, the propylene yield is superior in comparison with VTi5 catalyst. The catalyst activity can be correlated with maximum reduction temperature.

Deactivation of VTi5 and VTNT-5 as well as VTNT-15 were studied for 3,000 min time-on-stream. It was found that the activity of VTNT-5 catalyst remain unchanged while a decline in catalytic activity observed in VTi5 and VTNT-15 catalysts. The development of rutile was considered as being a major element in the deactivation of the investigated catalysts which is influenced by the presence of vanadium and reaction atmosphere.

1. Introduction

Propylene is one of the most important building blocks in different petrochemical and polymer processes. Propylene is mostly produced from high temperature steam cracking process. This process is quite an energy intensive process. Catalytic cracking, propane dehydrogenation, metathesis and methanol based processes (MTO or MTP) are the other propylene sources. As the propylene demand growth is large, development of alternative processes with lower energy consumption is of utmost importance. Oxidative dehydrogenation of propane (ODHP) is among proposed potential solutions to the aforementioned demand growth which is in contrast to nonoxidative pathways, presents no thermodynamic limitations and is a highly exothermic reaction [1–10].

Supported vanadium oxide (vanadia) is a commonly employed catalyst for several reactions and is most extensively studied in ODHP. Generally, bulky vanadium pentoxide demonstrates a relatively low catalytic performance for selective alkane oxidation. In other hand supporting on oxides such as titania, alumina, and etc., leads to development of catalysts with superior activity and selectivity [3,11]. Catalytic performance of the vanadia catalysts depends on the specific support, promoters, vanadia loading, calcination temperature, and etc. [1,2].

It is suggested that anatase supported vanadia catalysts are highly active in propane ODH. Nevertheless conventional anatase titania suffers from low surface area. Also relatively high temperatures and some impurities and additives induce the anatase to rutile phase transformation that creates disadvantages in terms of availability of active sites to the reactants. The presence of vanadia in the supported catalysts quickens sintering process and the anatase to rutile phase transformation [12–16].

Since the innovative work of Kasuga [17], TiO_2 and/or titanate nanotubes possessing large specific surface area and specific

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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 with an aqueous solution of NaOH in a mild temperature [18,19]. The process is cost-effective, simple, and environmentally friendly [18].

Active phases such as Au-Rh (single or bimetal) [20–22], V_2O_5 [23,24], CoMoS [25], WO_x [26], Pt nanocrystals [27], Pt-Ir [28], MoO_3 [29], and NiW [30] have been decorated on titanate and/or titania nanotubes. A number of these systems probed in a chemical reaction such that promising results reported by these authors.

Liu et al. [23] reported elaboration of a V_2O_5 catalyst supported on titanate nanotubes. They reported an improvement in methanol oxidation to dimethoxymethane selectivity as compared to TiO_2 P25 supported vanadia catalyst. Superior performance of vanadia deposited on sulfated TiO_2 nanotubes in comparison with sulfate-free nanotubes was reported in chlorobenzene total oxidation [31].

In this contribution, we present an alternative to conventional systems for the specific case of oxidative dehydrogenation process over VO_x/TiO_2 catalysts. Vanadia loading and calcination temperature effects on morphology and catalytic performance of vanadia supported on titanate nanostructures in oxidative dehydrogenation of propane is studied. Catalyst deactivation phenomena is considered in aforementioned reaction system on the nanostructured vanadia/titanate catalyst and compared to the conventional Degussa P25 supported vanadia catalyst.

2. Experimental

2.1. Fabrication of titanate nanotube

Typically, 1.7 g of Degussa TiO_2 P25 was added to 150 mL of 10 M aqueous solution of NaOH (Merck). The resulting mixture was stirred for 30 min, and transferred into a Teflon-lined stainless steel autoclave occupying about 80% of the volume. The sample maintained at 140 °C for 24 h after sealing the container. The resulting material cooled to room temperature then subjected to centrifugation and washing with a diluted acid using 0.1 M HNO_3 solution. The washing process continued until the pH of the rinsing solution reached about 1. The precipitates then washed with distilled doubly deionized water until the washing solution achieved pH 7. The acid-treated sample was oven-dried at 110 °C overnight.

2.2. Catalyst preparation

The incipient wetness impregnation method utilized in the preparation of catalysts. Two types of catalysts were prepared and investigated. The catalysts are referred to VTi5 for 5 wt.% V_2O_5 supported on TiO_2 P25 and VTNT-x, which stands for x wt.% V_2O_5 supported on titanate nanotube. Briefly, a measured amounts of ammonium metavanadate and oxalic acid (molar ratio = 1/2) were added to calculated volume of deionized water correspond to the total pore volume of the support. The stirring continued at 70 °C until dark blue solution appeared. Then, the support was added to the solution. After forming a paste the resulting sample aged for about 5 h followed by oven-drying at 110 °C overnight. Once dry, the powder was calcined in static air at 500 °C. After cooling to room temperature, the calcined sample went through forming process and 60–100 mesh size was taken for the catalytic activity and deactivation tests.

2.3. Catalyst characterization

The specific surface areas (S_{BET}) of the prepared catalysts were determined at the liquid nitrogen temperature (77 K) from the adsorption and desorption isotherms of N_2 using a Quantachrome CHEMBET-3000 apparatus.

The FTIR spectra acquired using a Fourier transform spectrometer (Spectrum 2000, PerkinElmer) in the wavenumbers range of 450–4000 cm^{-1}.

The H_2-temperature programmed reduction (H_2-TPR) experiments were carried out in the same instrument as BET using 20 mg of samples by 10 sccm of 7.0% H_2 in Ar with concomitant temperature leveling up to 950 °C with a heating rate of 10 °C/min. A thermal conductivity detector (TCD) monitored the hydrogen consumption by analyzing the TPR reactor effluent. For the quantitative purposes, the TCD signal was calibrated by reduction of Ag_2O under similar conditions as of the H_2-TPR experiments of the samples.

X-ray diffraction (XRD) patterns of the prepared samples were obtained with a Philips PW1800 diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm). The intensities were determined over an angular range of $5° < 2\theta < 70°$ for all the prepared samples with a step-size $\Delta(2\theta)$ of 0.03° and a count time of 2 s per step. The indexation of the acquired spectra carried out by comparison with the JCPDS files (joint committee on powder diffraction standards).

The mean crystallite size of the sample was estimated employing the Scherrer's equation, from XRD line-broadening measurement:

$$d_{XRD} = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is a constant equal to 0.9 (shape factor), λ is the wavelength of the used X-ray in nanometer, θ is the diffraction angle and β is the true half-peak width.

X-ray photoelectron spectroscopy (XPS) spectra were obtained with a vacuum generator at 10^{-8} Torr using Al Kα radiation ($h\nu = 1486.6$ eV). Prior to the analysis, the samples were out gassed at room temperature in a preparation chamber. The binding energies were calibrated based on the hydrocarbon C 1s peak at 285 eV. After subtracting the Shirley-type background, core level spectra of the Ti 2p, V 2p, and O 1s were curve-fitted, maintaining the chi square value less than 2.

Laser Raman spectroscopy (LRS) were recorded with a Bruker (model SENTERRA (2009)) spectrophotometer. A diode laser ($\lambda = 785$ nm) that operated at 25 mW was employed as Raman excitation source and a germanium thermoelectrically cooled charged couple device (Andorf) as detector.

Scanning electron microscopy (SEM) was done by a Philips XL30 apparatus to determine the morphology of the prepared samples.

TEM measurements were carried out on transmission electron microscope "JEOL" JEM-2100 (200 kV) equipped with an analytical system for energy dispersive X-ray spectrometry (EDS). For TEM measurements the samples were grounded, suspended in isopropanol at room temperature and dispersed by ultrasonic agitation. Then, an aliquot of the prepared solution was dropped on a 3 mm diameter lacey carbon copper grid.

2.4. Catalytic activity and deactivation study

Oxidative dehydrogenations of propane experiments were carried out in a microflow fixed-bed down-flow reactor with inner-diameter of 6 mm and outer-diameter of 7 mm at atmospheric pressure. The reactor was heated in an electric furnace with a K-type thermocouple that was inserted in the catalytic bed. Blank runs were conducted without catalyst using a reactor packed with quartz wool at 500 °C. The results showed negligible propane conversion at the feed conditions studied confirming the insignificancy of gas-phase reactions. For each test about 160 mg of catalyst with a mesh size of 60–100 was taken and homogeneously diluted with 160 mg silicon carbide with a mesh size of 40. The samples were held on a plug of quartz wool. The catalysts were pretreated in 20 sccm 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