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A novel nanoengineered VO_x catalyst supported on highly ordered TiO_2 nanotube arrays for partial oxidation reactions

Jose E. Herrera*, Tayirjan T. Isimjan, Inusa Abdullahi, Ajay Ray, Sohrab Rohani

Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, N6A 5B9, Canada

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ABSTRACT

A new class of nanoengineered partial oxidation catalyst has been prepared through the use of chemical vapor deposition of a vanadium oxide precursor over a highly ordered TiO_2 nanotube array. A battery of characterization techniques including X-ray diffraction (XRD) together with scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman, and DRS-UV/vis indicate that the vanadia species are extremely well dispersed onto the surface of the nanotube array. Studies of the catalytic activity of this material were performed using the partial oxidation of ethanol as a probe reaction and compared with those obtained using typical P-25 TiO_2 powdered support. Results showed that the nanoengineered approach to catalyst fabrication leads to a highly active catalytic material where most of the vanadium oxide phase is located on the surface and accessible for catalysis.

1. Introduction

Catalytic systems based on vanadium oxides are known to be highly active and selective for a number of industrially relevant chemical transformations. It has already been established that the catalyst support plays an important role in both the activity and selectivity [1–4]. Several particle supported V_2O_5 catalyst formulations have been tested in important industrial scale processes such as selective oxidation [5–7], ammoxidation of hydrocarbons [8], and selective reduction of NO_x with NH_3 in the presence of O_2 [9]. Al_2O_3, SiO_2, TiO_2 and ZrO_2 nanoparticles are commonly used as supports for these catalysts [6,7,10–12]. Among these, titanium oxide, leads to an enhancement of the catalytic properties of vanadium oxide [13–16]. However, variations on the available surface area of TiO_2 powder supports present challenges for a uniform surface coverage of vanadium oxide and creates disadvantages in terms of availability of active sites to the reactants [17].

In this contribution, we present an alternative to conventional systems for the specific case of partial oxidation process over VO_x/TiO_2 catalysts. This novel methodology is based on the use of a flat substrate of highly ordered TiO_2 nanotube arrays as support for vanadium oxide. Due to its highly ordered vertical orientation this material presents advantages over conventional VO_x/TiO_2 systems such an availability of accessible surface area for catalysis and a potentially uniform coverage of VO_x catalytic species on the surface support achieved under the right VO_x deposition conditions. In combination with a vanadia chemical vapor deposition this approach leads to the fabrication of a highly active thin layer of vanadium oxide anchored on titanium oxide nanotubes which are in turn anchored to a titanium flat surface. The use of a titanium flat surface is an attractive alternative porous to particles. The substrate shares the advantages of flat surfaces such as uniformity and suitability for surface studies and also offers a large accessible area for increased active species loading. Moreover, these materials represent a family of catalysts based on flat surfaces that are able to perform at the same level as conventional powdered catalysts. Most of flat surface catalytic materials currently described in the literature are presented as model systems that can only be used to carry fundamental studies, normally at very low pressures [18]. The fact that these VO_x coated TiO_2 supported nanotube arrays are able to carry out catalytic reactions under similar conditions as those used for traditional particle-based systems further advances catalytic technology.

* Corresponding author. Tel.: +1 519 661 2111x81262; fax: +1 519 661 3498.
E-mail addresses: jherrer3@uwo.ca, jherrera@eng.uwo.ca (J.E. Herrera).

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