Catalysis Today 263 (2016) 84–90

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Oxidative dehydrogenation of isobutane over vanadia catalysts supported by titania nanoshapes

Shannon Kraemer, Adam J. Rondinone, Yu-Tong Tsai, Viviane Schwartz,
Steven H. Overbury, Juan-Carlos Idrobo, Zili Wu*

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form 4 September 2015
Accepted 16 September 2015
Available online 2 November 2015

Keywords:
Titania
Vanadia
Support effect
Nanoshapes
Surface facets
Surface structure
Oxygen vacancy formation energy
Isobutane oxidative dehydrogenation
Raman spectroscopy

ABSTRACT

Support plays a complex role in catalysis by supported metal oxides and the exact support effect still remains elusive. One of the approaches to gain fundamental insights into the support effect is to utilize model support systems. In this paper, we employed for the first time titania nanoshapes as the model supports and investigated how the variation of surface structure of the support (titania, TiO_2) impacts the catalysis of supported oxide (vanadia, VO_x). TiO_2 truncated rhombi, spheres and rods were synthesized *via* hydrothermal method and characterized with XRD and TEM. These TiO_2 nanoshapes represent different mixtures of surface facets including [1 0 1], [0 1 0] and [0 0 1] and were used to support vanadia. The structure of supported VO_x species was characterized in detail with *in situ* Raman spectroscopy as a function of loading on the three TiO_2 nanoshapes. Oxidative dehydrogenation (ODH) of isobutane to isobutene was used as a model reaction to test how the support shape influences the activity, selectivity and activation energy of the surface VO_x species. It was shown that the shape of TiO_2 support does not pose evident effect on either the structure of surface VO_x species or the catalytic performance of surface VO_x species in isobutane ODH reaction. This insignificant support shape effect was ascribed to the small difference in the surface oxygen vacancy formation energy among the different TiO_2 surfaces and the multi-faceting nature of the TiO_2 nanoshapes.

1. Introduction

Supported metal oxides are a class of catalysts widely used in industry for a variety of reactions [1]. For example, the Philip catalyst, supported chromium oxide, has been used in direct dehydrogenation (DH) of alkane to alkene [2]. Based on thermodynamic consideration, oxidative dehydrogenation (ODH) is favored over DH for the conversion of alkane to alkene due to the formation of water [3]. However, the addition of oxidant, normally O_2, also brings about the challenge of selectivity control between alkene and the total oxidation products such as CO and CO_2. Therefore, strong research interest has been attracted in academia in developing active and selective alkane ODH catalysts among which supported vanadia is currently the most studied catalysts [1,4–6].

In addition to the extensive efforts devoted to understand the catalytic effect of the structure of surface vanadia (VO_x) [1,4,7,8], the support materials were also found to play a profound effect on the performance of vanadia catalysts in alkane ODH [6,9,10]. Current research has been exclusively concentrated on the effect of support compositions that are generally classified as reducible and non-reducible. It was shown that composition variation of support materials can result in several orders of magnitude difference in reactivity of surface VO_x species in alcohol oxidation and alkane ODH reactions [1,4,6,9]. This was mostly ascribed to the difference in the electronegativity of the interface bond, V–O–M (M stands for the metal atom in the metal oxide support) in the supported VO_x catalysts [1,9]. However, the change in composition of the supports can inevitably be complicated by the variation of surface structure of the supports. Thus the support effect in supported VO_x catalysts still remains elusive.

One approach to better understand the support effect is to separate the composition effect from the surface structure effect of the supports. By tuning the shape while keeping the composition unchanged for ceria support, we recently showed that through the variation of surface structure of ceria, rods *vs.* octahedra, the supported VO_x exhibits appreciable difference in reaction activation energy and activity in ODH of isobutane [11]. This support shape effect was mainly ascribed to the surface structure dependence

---

* Corresponding author. Tel.: +1 865 576 1080.
E-mail address: wuz1@ornl.gov (Z. Wu).

http://dx.doi.org/10.1016/j.cattod.2015.09.049
0920-5861/Published by Elsevier B.V.

of oxygen vacancy formation energy of the ceria rods and octahedra. It was suggested that the reactivity of supported VO_x could be correlated to the oxygen vacancy formation energy of the supports [6,12,13], *i.e.*, the less the energy needed to form O-vacancy on the support, the lower the activation energy is for the rate-determining step, C-H bond cleavage, in alkane ODH [12,13]. With the increasing availability of various metal oxide nanoshapes [14–17], it is possible to extend to other nanoshaped oxides as supports for VO_x to investigate if the support shape effect is a general phenomenon. Surprisingly, the VO_x/CeO_2 nanoshape system, also employed by other research groups [18,19], was the first and only example being investigated for the surface structure effect of oxide support on the catalytic performance of VO_x. No other nanoshaped oxides have been utilized to support VO_x and tested for catalytic reactions. In this paper, three titania nanoshapes, truncated rhombi (TiO_2-tr), rods (TiO_2-r) and spheres (TiO_2-s), were used to support VO_x and tested for ODH of isobutane for the first time to understand TiO_2 shape effect in vanadia catalysis. In contrast to VO_x/CeO_2 nanoshape case, no evident support shape effect was observed for these VO_x/TiO_2 catalysts in isobutane ODH and the possible reasons were discussed.

2. Experimental methods

2.1. Material synthesis

The titania nanoshapes were synthesized *via* a modified solvothermal method reported by Dinh et al. [20]. Briefly, different ratio of titanium butoxide (TB), oleic acid (OA) and oleyl amine (OM) were mixed in absolute ethanol and heated in an autoclave at different temperatures and durations for the three titania nanoshapes. For example, to synthesize TiO_2 with truncated rhombic (TiO_2-tr) shape, 7.5 mmol of TB was added to a mixture of 15 mmol OA, 60 mmol OM and 150 mmol absolute ethanol. The obtained mixture was transferred into a 100 mL Teflon-lined stainless autoclave cell containing 30 mL mixture of ethanol and water (96% ethanol, v/v). The system was then heated to 453 K and kept for 18 h. For rod (TiO_2-r) and sphere (TiO_2-tr) shaped TiO_2, the TB:OA:OM ratio was respectively 1:8:2 and 1:6:4 and the solvothermal temperature was 413 and 453 K, respectively. The holding time was both 18 h. After the reaction was cooled down to room temperature, the obtained precipitates were washed with water and ethanol 3 times and then vacuum dried at 323 K overnight. According to the thermal gravimetric analysis (TGA) (see Fig. S1 in Supporting information), the organic surfactants on the titania can be removed in air at 673 K. So the samples were finally calcined at 673 K in air for 4 h to obtain clean TiO_2 surfaces.

The VO_x/TiO_2 samples were prepared *via* incipient-wetness impregnation of TiO_2 nanoshapes with 2-propanol solutions of vanadium isopropoxide ($VO(O\text{-}Pr^i)_3$, Alfa-Aesar 95–99% purity) in a Schlenk line. Typically, pre-calcined TiO_2 powder was loaded into a fritted reactor, which was sealed with a rubber septum at one end and connected to a Schlenk line at the other end. The initially loaded sample was evacuated at 523 K for 1 h and cooled down to room temperature before switching to nitrogen atmosphere. Through a syringe, 10 mL of anhydrous 2-propanol (Aldrich, 99.8%) and a weighed amount of vanadium isopropoxide were transferred into the reactor. The solution was stirred overnight at room temperature and dried *via* vacuum filtration. The impregnated powder was switched to nitrogen flow and further dried in the reactor at 523 K for 1 h before cooling down and exposing to air. The sample was transferred to an oven and calcined in air at 573 K for 1 h and then at 673 K for 4 h. A VO_x/TO_2 sample with surface VO_x density of Y V/nm^2 is denoted as YV/TO_2 in the paper. The content of VO_x in the samples was analyzed with X-ray fluorescence (XRF) method.

2.2. Material characterizations

Transmission electron microscopy (TEM) images of various TiO_2 and VO_x/TiO_2 samples were performed using a Zeiss Libra 120 system operating at 120 kV. The NION UltraSTEM 100 was used to obtain the high resolution image of the TiO_2 nanoshapes. Powder X-ray diffraction (XRD) was performed on a Panalytical X'Pert Pro MPD, using Cu Kα radiation and Bragg-Brentano geometry. Brunauer–Emmett–Teller (BET) surface area of the 673 K calcined TiO_2 nanocrystals was measured *via* nitrogen adsorption at 77 K by using a Micromeritic Gemini 275 system. Thermal gravity analysis was done on a TA TGA Q500 system. The as-synthesized TiO_2 samples were heated in an air flow (20 mL/min) and ramped at 10 K/min to 1073 K to follow weight loss.

2.3. Raman spectroscopy

The VO_x/TiO_2 samples were dehydrated *in situ* in a Raman catalytic reactor (Linkam CCR1000) before Raman spectral collection at room temperature. The dehydration was done by heating the sample (ca. 20 mg) in flowing 5% O_2/He (30 mL/min) from room temperature to 673 K (ramping rate 10 K/min) and holding there for additional 1 h. The sample was then cooled down in the same atmosphere to 393 K for spectra collection. Raman scattering from the sample was collected *via* fiber optics connected directly to the spectrograph stage of a triple Raman spectrometer (Princeton Instruments Acton Trivista 555) [21]. Edge filters (Semrock) were used in front of the UV–vis fiber optic bundle (Princeton Instruments) to block the laser irradiation. The 325 and 442-nm excitations (5 mW at sample) are obtained from a HeCd laser (Melles Griot) and the 532-nm excitation (20 mW at sample) is emitted from a solid-state laser (Princeton Scientific, MSL 532-50). The laser spot size is ca. 50 ~150 μm depending on the laser wavelength used. A UV-enhanced liquid N_2-cooled CCD detector (Princeton Instrument) was employed for signal detection. The Raman reactor was placed on an XY stage (Prior Scientific, OptiScan XY system), which translates in raster mode while collecting the spectra. The fast translation has shown been able to eliminate/minimize any laser damage of the samples. Cyclohexane solution was used as a standard for the calibration of the Raman shifts.

2.4. Oxidative dehydrogenation of isobutane

The catalytic performance test for isobutane ODH reaction was carried out at atmospheric pressure in a packed bed stainless steel autoclave reactor (PID Eng & Tech, Spain) [22]. Typically, 0.1 g of VO_x/TiO_2 catalyst mixed with 0.3 g of quartz sand was placed in a vertically positioned stainless steel tubular reactor under atmospheric pressure for the reaction tests. The feed composition for the reaction consisted in a flow mixture of 4% i-C_4H_{10}/He and 5% O_2/He and the flows were tuned in order to keep an isobutane/oxygen ratio of 2/1. Prior to the reactivity test, the catalyst was pre-treated at 673 K in 5%O_2/He for 1 h. The catalyst was then cooled down to 548 K in 5%O_2/He and exposed to the reaction mixture. The reaction was run at different temperature up to 648 K at a fixed space velocity of 16,800 mL/(h g_{cat}) to vary the conversion so that the activation energy can be obtained. The conversion level is controlled generally lower than 10%. The flows were also varied from 8,400 to 33,600 mL/(h g_{cat}) in order to study the reaction at different space velocities but at a fixed reaction temperature of 573 K. The reactants and products were analyzed using an on-line gas chromatography conducted on an Agilent 6890N Gas Chromatography system with a Hayesep N column and a molecular sieve column. CO and CO_2 were converted to CH_4 through a methanizer before they passed through a flame ionization detector for analysis. Isobutene, CO, and CO_2