Oxidative Dehydrogenation of Isobutane over Vanadia Catalysts

Supported by Titania Nanoshapes

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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 [101], [010] and [001] 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.

Key Words: titania, vanadia, support effect, nanoshapes, surface facets, surface structure, oxygen vacancy formation energy, isobutane oxidative dehydrogenation, Raman spectroscopy

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 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 ($\text{TiO}_2\text{-tr}$), rods ($\text{TiO}_2\text{-r}$) and spheres ($\text{TiO}_2\text{-s}$), 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 ($\text{TiO}_2\text{-tr}$) 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 ($\text{TiO}_2\text{-r}$) and sphere ($\text{TiO}_2\text{-tr}$) 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 **Figure 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 ($\text{VO}(\text{O-Pri})_3$, 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/TiO_2 sample with surface VO_x density of $Y \text{ V/nm}^2$ is denoted as $Y\text{V}/\text{TiO}_2$ 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 NIONUltraSTEM 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 $\text{Cu K}\alpha$ 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, MSL532-50). The laser spot size is ca. 50 ~150 μm depending on the laser wavelength used. A UV-enhanced liquid N₂-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/TiO₂ 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-C₄H₁₀/He and 5% O₂/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% O₂/He for 1 h. The catalyst was then cooled down to 548 K in 5% O₂/He and exposed to the reaction mixture. The reaction was run at different temperature up to 648 K at a fixed space velocity of 16800 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 8400 to 33600 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 CO₂ were converted to CH₄ through a methanizer before they passed through a flame ionization detector for analysis. Isobutene, CO, and CO₂ were the only products detected. In all tests, carbon mass balances were within 100 ± 1%.

3. Results and Discussions

3.1. XRD, TEM, and BET analysis of TiO₂ nanoshapes and VO_x/TiO₂

Figure 1 shows the XRD patterns of the three TiO₂ polymorphs. They all can be indexed to the pure anatase structure with similar crystallinity as indicated by the peak positions and width. The particle size, determined from a Williamson-Hall plot, is 11 nm for truncated rhombic TiO₂ (TiO₂-tr), 10 nm for spherical TiO₂ (TiO₂-s), and 6 nm for TiO₂ rods (TiO₂-r). The size obtained from XRD is consistent with the following TEM results for the three TiO₂ nanoshapes. The XRD pattern of a VO_x/TiO₂ sample with the highest VO_x loading (6.7V/nm²) is the same as the parent TiO₂ support, and there is no detectable crystalline V₂O₅ formed. **Figure 2** shows the TEM images of the TiO₂ nanocrystals. The TiO₂-tr (**Figure 2a, 2b**) particles are about 10 nm across and 20 – 50 nm long. The high resolution TEM image of a single truncated rhombic TiO₂ shows good crystallinity and suggests that the particle is enclosed by eight {101} facets, two {001} and four {010} facets according to Wulff construction [23, 24]. The TiO₂-s particles (**Figure 2c**) range from 8 to 20 nm in diameter, enclosed likely with a mixture of {001}, {010} and {101} facets according to the geometry. Since {101} is the most thermodynamically stable

surface[23, 25], the TiO₂-s might be dominated by this facet. The rod-shaped TiO₂ (**Figure 2d**) is homogenous in diameter (~6 nm) but rather heterogeneous in length, ranging from 10 to 40 nm. According to the TEM image and the crystallographic symmetry of anatase, the TiO₂-r can be identified as terminated with {010} on the side and {001} at both ends[24, 26] with the proportion of {010} facet being generally larger than {001}. The TEM observations are in good accordance with previous report of the titania nanomaterials [20, 26], indicating successful synthesis of the desired morphology of TiO₂ crystals in our study. The BET areas of the TiO₂ truncated rhombi, spheres and rods are 93, 103 and 110 m²/g, respectively.

VO_x was supported on the three TiO₂ nanoshapes via impregnation method with three different loadings. Considering the difference in surface area of the three TiO₂, the VO_x loading is expressed in terms of surface VO_x density (V/nm²): 0.7, 2.4 and 6.7 V/nm². These loadings are below the monolayer value of vanadia species dispersed on titania surface[27], as confirmed by the XRD and the following Raman results where no crystalline V₂O₅ is observed. There is no obvious change of shape of the TiO₂ supports after VO_x loading as indicated by the TEM images (**Figure S2**). The BET area of the VO_x/TiO₂ samples is shown in **Table S1** as well as the particle size estimated from XRD measurements. In general, the particle size of the VO_x/TiO₂ is quite similar to the parent TiO₂ support while the surface area decreases slightly as more VO_x is supported on the surface.

3.2. Raman spectroscopy of the structure of dehydrated VO_x/TiO₂

The structure of surface VO_x species in the VO_x/TiO₂ samples was characterized with in situ Raman spectroscopy under dehydrated condition. As it was shown in other supported

VO_x systems that a certain laser excitation is preferred for characterizing the surface VO_x species as the support shows optical absorption across the UV-Vis region [21, 28, 29]. In order to screen for the proper laser excitation, three laser excitations at 325, 442 and 532 nm were utilized to characterize the VO_x/TiO₂ sample and the spectra for 6.7V/TiO₂-r were as an example in **Figure 3** from 700 to 1200 cm⁻¹ region. The spectral contour is quite different for the three spectra. The V=O stretching mode at 1030 cm⁻¹ is quite evident in the 532 and 442-nm excited spectra while it appears as a weak shoulder on the slope in the 325-nm spectrum. In contrast, 325-nm excitation gives more pronounced features in the range 750 ~ 1000 cm⁻¹ than the 442 and 532-nm excitations. The two broad bands centered around 860 and 927 cm⁻¹ can be assigned to the bridging modes of V-O-Ti and V-O-V. [30-34] Apparently, UV excitation is more sensitive to the bridging modes while visible excitation is favored for the terminal vanadyl mode of VO_x species in the VO_x/TiO₂ system. We choose 442 nm excitation for the rest of the study as it is sensitive to both bridging V-O- and terminal V=O modes.

The Raman spectra for VO_x/TiO₂-tr are shown in **Figure 4A** as a function of surface VO_x density. The bare TiO₂-tr exhibits Raman bands at 398, 546 and 641 cm⁻¹, characteristic of anatase phase [34, 35]. The 0.7V sample gives a new band at 1026 cm⁻¹, due to V=O stretching [34, 36-38] and a slightly elevated slope in the range 750 ~ 1000 cm⁻¹ on TiO₂ background. Both features increase in intensity relative to those of TiO₂ with increasing of VO_x density to 2.4 and 6.7 V/nm². To minimize the background from TiO₂ in the region 750 ~ 1000 cm⁻¹, the Raman spectra of the three VO_x/TiO₂-tr are subtracted by the TiO₂ spectrum and the resulting difference spectra are shown in **Figure 4B**. The subtraction makes the Raman bands due to surface VO_x species clearly resolved. The V=O mode moves from 1026 to 1033 cm⁻¹ from 0.7V to 6.7V, due to the increased polymerization degree of surface VO_x species [8, 30, 39-41]. The main peak of

the broad feature appears at around 903 cm^{-1} on 0.7V sample, then moves to 912 cm^{-1} for 2.4V and 922 cm^{-1} for 6.7V. A second feature at around 865 cm^{-1} can be discerned when the surface VO_x density increases. Considering the increase of the 865 cm^{-1} feature relative to the 922 cm^{-1} one as a function of VO_x loading, it appears that the broad band above 900 cm^{-1} ($903 \sim 922\text{ cm}^{-1}$) may be ascribed to V-O-Ti mode while the one at around 865 cm^{-1} to V-O-V mode. Assignment of the broad band at around 930 cm^{-1} to V-O-V mode was also made in previous studies of VO_x/TiO_2 systems[27, 30-33]. No Raman bands characteristic of crystalline V_2O_5 can be observed even on the 6.7V sample, indicating a high dispersion nature of the surface VO_x species.

The Raman spectra of dehydrated VO_x/TiO_2 -s and VO_x/TiO_2 -r are shown respectively in **Figure 5A** and **Figure 5B** as a function of surface VO_x density. The TiO_2 spheres and rods are also clearly in anatase phase as characterized by the Raman bands at $398, 546$ and 641 cm^{-1} . Upon loading of VO_x , the surface structure evolution of VO_x is quite similar on the two TiO_2 nanoshapes and closely resembles that of VO_x/TiO_2 -tr (**Figure 4**). Namely, the V=O stretching mode is observed at around 1028 cm^{-1} at low vanadia loading, shifting to higher Raman shift with VO_x surface density, 1030 cm^{-1} at 2.4 V/nm^2 and 1032 cm^{-1} at 6.7 V/nm^2 . The bridging modes of V-O-Ti and V-O-V in the range $750 \sim 1000\text{ cm}^{-1}$ grow in intensity relative to the V=O mode as the VO_x density increases, consistent with the increasing polymerization degree of the surface VO_x species as more vanadia is loaded on the TiO_2 surface. Again, no characteristic Raman bands for V_2O_5 can be observed on the highest loading samples, suggesting a complete dispersion of VO_x on the TiO_2 support.

Summarizing the Raman results of the three VO_x/TiO_2 systems, the structure of surface VO_x species is very similar on the three TiO_2 nanoshapes at similar surface VO_x density, i.e.,

VO_x species exist in less polymerized form at low surface density and in more polymerized structure at high surface density. All VO_x species are in highly dispersed form without the formation of crystalline V₂O₅. The three TiO₂ nanoshapes are in anatase phase and the anchoring of VO_x does not change the bulk structure of the TiO₂ support.

3.3. Oxidative dehydrogenation of isobutane over VO_x/TiO₂

The three VO_x/TiO₂ nanoshape systems were tested for isobutane ODH reaction in the temperature range of 548 to 648 K. The structure effect of both the surface VO_x and the TiO₂ support was investigated. To study the structural effect of surface VO_x species, the surface density of VO_x was varied (0.7, 2.4 and 6.7 V/nm²) to change the surface structure of VO_x species while the support shape was fixed by using TiO₂-tr. The catalytic performance of the three VO_x/TiO₂-tr samples in isobutane ODH is displayed in **Figure 6A** where the Arrhenius plots are shown. Despite the different polymerization degree of the surface VO_x species on the 0.7V, 2.4V and 2V samples, the activation energy is about the same on these samples (~ 58 kJ/mol), suggesting that the catalysts share a similar active center, most likely the V-O-Ti site [1, 7]. The reaction rate (turnover frequency, s⁻¹) was calculated by dividing the converted isobutane (mol) per second with the total amount of V (mol) since all VO_x are highly dispersed on the surface as indicated by the Raman study. There is a slight variation of the reaction rate among the three catalysts when compared at the same reaction temperature. The selectivity to isobutene over the three catalysts is plotted vs. conversion in **Figure 6B**. Due to the inability to control the space velocity in a wide range in our reaction system, the conversion level was different on the three samples. A general trend is that the higher the conversion, the lower the selectivity is for

isobutene. It does not appear there is a strong dependence of selectivity on the surface structure VO_x species on the VO_x/TiO_2 -tr catalysts.

Next, the structure effect of the support surface was studied by varying the TiO_2 shapes while keeping the surface VO_x density at similar level. The intermediate VO_x surface loading, i.e., $2.4\text{V}/\text{nm}^2$, was chosen for the comparison. The Raman spectra (**Figure S3**) of the three samples are very close to each other. E.g., the $\text{V}=\text{O}$ stretching is at the same frequency (1030 cm^{-1}), suggesting a very similar structure of the polymerized VO_x species on the three TiO_2 nanoshapes. **Figure 7A** compares the activation energy and reaction rate of isobutane ODH for 2.4V supported on the three TiO_2 nanoshapes. The activation energy varies in a narrow range $57 \sim 62\text{ kJ/mol}$ on the three catalysts. So is the reaction rate: ranging from $2.8\text{E-}4$ to $4.5\text{E-}4\text{ s}^{-1}$ as measured at reaction temperature of 573 K . The selectivity to isobutene on the three 2.4V samples is shown in **Figure 7B** as a function of conversion at 573 K . The $2.4\text{V}/\text{TiO}_2$ -s sample exhibits marginally higher selectivity than the other two samples at similar conversion level. Overall, **Figure 7** shows almost independence of catalytic performance of the VO_x in isobutane ODH on the shape of the TiO_2 supports.

3.4. General comment on the support shape effect

The lack of obvious support effect on the catalysis of VO_x/TiO_2 system is in contrast to the VO_x/CeO_2 system[18, 29] where evident support effect was found on the catalysis of VO_x in ODH reactions. We propose that this could be ascribed mostly to the surface oxygen vacancy formation energy, which does not vary significantly among the different TiO_2 surfaces. As pointed out earlier, it was proposed that the rate-determining step (rds) of alkane ODH is the

removal of the second H via interacting with the surface oxygen[11-13]. So the lower the oxygen vacancy formation energy is for the catalyst, the easier the ODH reaction is expected to proceed. The oxygen vacancy formation energy of TiO_2 surfaces was computed to be: (101): 4.7 eV > (010): 4.4 eV > (001): 4.38 eV[25]. The absolute energy is much larger than that for the ceria facets ((111): 2.60 eV > (100): 2.27 eV > (011): 1.99 eV) [42]. Furthermore, when compared to the absolute oxygen vacancy formation energy, the difference in the oxygen vacancy formation energy among the TiO_2 facets is not as significant as that among the ceria facets. Therefore, the isobutane ODH is more difficult on VO_x/TiO_2 system than on VO_x/CeO_2 and the rate-determining step of this reaction may not be sensitive enough to probe the small energy difference among the various TiO_2 facets when the needed total reaction energy (absolute oxygen vacancy formation energy) is already quite high. A further complicating factor is that the three TiO_2 nanoshapes are not mono-faceted. For example, the truncated rhombic TiO_2 is enclosed by 8 [101], 4 [010] and 2 [001]; the rods are terminated by a mixture of [010] and [001]; the spherical nanocrystals are likely a combination of various TiO_2 facets. This mixing nature of the surface facets along with the small difference in surface oxygen vacancy formation energy of the three TiO_2 nanoshape supports work in accordance so that no obvious support shape effect is exhibited in the ODH reaction over the VO_x/TiO_2 nanoshapes. Further study of VO_x/TiO_2 system utilizing mono-faceted titania nanoshapes may be warranted to explore the support shape effect of TiO_2 nanocrystals in redox type reactions.

4. Conclusions

There TiO_2 nanoshapes, truncated rhombi, spheres and rods have been used to support VO_x and tested for ODH of isobutane to investigate support shape effect in oxide catalysis. It was shown that the surface VO_x species are highly dispersed on TiO_2 surface and the polymerization degree rises with the increase of surface VO_x loading. The structure of VO_x species is similar on the different TiO_2 nanoshapes at comparable VO_x density. The TiO_2 supports do not show noticeable shape effect on the activity, selectivity and activation energy of the VO_x species in ODH reaction of isobutane, which can be attributed mostly to the small differences in the surface oxygen vacancy formation energy of the exposed TiO_2 facets, [101], [010] and [001] and also the multi-faceting nature of the three TiO_2 nanoshapes.

Supporting Information.

The TGA plots for TiO_2 , TEM images of 6.7V/ TiO_2 nanoshapes, and a comparison of Raman spectra of dehydrated 2.4V/ TiO_2 nanoshapes are available in the supporting information.

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Notes

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Figure Captions

Figure 1. XRD patterns of TiO₂ nanoshapes and 6.7V/TiO₂-tr.

Figure 2. TEM and HRSTEM of TiO₂ nanoshapes: truncated rhombi (a,b), rods (c) and spheres (d).

Figure 3. Raman spectra of dehydrated 6.7V/TiO₂-r at 393 K collected with three different laser excitations: 325, 442 and 532 nm.

Figure 4. Raman spectra of dehydrated VO_x/TiO₂-tr collected at 393 K. (A) is with the TiO₂-tr support spectrum shown and (B) gives the difference spectra after subtracting the TiO₂ spectrum from the VO_x/TiO₂ spectra.

Figure 5. Raman spectra of dehydrated (A) VO_x/TiO₂-s and (B) VO_x/TiO₂-r collected at 393 K.

Figure 6. (A) Arrhenius plots of three VO_x/TiO₂-tr samples for isobutane ODH in the temperature range 548 to 648 K. (B) Selectivity to isobutene vs. conversion plots for three VO_x/TiO₂-tr samples in isobutane ODH at 573 K.

Figure 7. (A) Activation energy and reaction rate of three 2.4V/TiO₂ nanoshapes for isobutane ODH at 573 K. (B) Selectivity to isobutene vs. conversion plots for three 2.4V/TiO₂ nanoshapes in isobutane ODH at 573 K.

Figure 1. XRD patterns of TiO_2 nanoshapes and 6.7V/ TiO_2 -tr.

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Figure 3. Raman spectra of dehydrated 6.7V/TiO₂-r at 393 K collected with three different laser excitations: 325, 442 and 532 nm.

Figure 4. Raman spectra of dehydrated $\text{VO}_x/\text{TiO}_2\text{-tr}$ collected at 393 K. (A) is with the $\text{TiO}_2\text{-tr}$ support spectrum shown and (B) gives the difference spectra after subtracting the TiO_2 spectrum from the VO_x/TiO_2 spectra.

Figure 5. Raman spectra of dehydrated (A) $\text{VO}_x/\text{TiO}_2\text{-s}$ and (B) $\text{VO}_x/\text{TiO}_2\text{-r}$ collected at 393 K.

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Graphic Abstract