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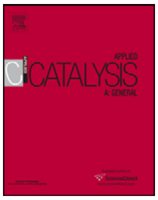

Effect of preparation method on nature and distribution of vanadium species in vanadium-based hexagonal mesoporous silica catalysts: Impact on catalytic behavior in propane ODH

Roman Bulánek*, Pavel Čičmanec, Hsu Sheng-Yang, Petr Knotek, Libor Čapek, Michal Setnička

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic

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ABSTRACT

This work reports comparative study of catalytic performance of VO_x-HMS catalysts prepared by ethanolic impregnation method and direct synthesis. In order to detailed investigation of vanadium speciation depending on vanadium content and its impact on catalytic behavior in C3–ODH, number of samples in wide range of vanadium content (1–16 wt.%) was prepared by both types of preparation. Prepared catalysts were tested in the oxidative dehydrogenation of propane at 540 °C under different contact times and catalytic results were correlated with physicochemical characteristics of the catalysts examined by XRD, XRF, SEM, N_2 adsorption/desorption isotherms, H_2-TPR and DR-UV–visible spectroscopy. Study led to conclusion, that (i) both monomeric VO_x complexes and oligomeric VO_x complexes with tetrahedral coordination containing V—O—V bonds are active and selective catalytic sites for C3–ODH, (ii) active VO_x species are characterized by distinct reduction peak in H_2-TPR pattern centered at 570–590 °C, (iii) VO_x-HMS vanadosilicates can be directly synthesized under ambient conditions without need for autoclave in wide range of vanadia loading with preservation of good catalytic performance and (iv) the catalytic results in C3-ODH were significantly better for synthesized catalysts compared to impregnated catalysts resulting in three times higher propene productivity of the best synthesized catalyst compared to the best impregnated one under the same reaction conditions. The higher is vanadium loading the more distinct is the difference in catalytic performance of both types of catalysts.

1. Introduction

Oxidative dehydrogenation (ODH) of alkanes provides a thermodynamically accessible route to the synthesis of alkenes from alkanes. A large number of reviews dealing with the ODH of light alkanes have been published since early 1990s [1–7]. A general feature of the most catalytic systems in ODH is that the selectivity to alkenes decreases with the increase of alkane conversion. In order to avoid the primary product over-oxidation of the alkane activation, it is necessary to develop highly structured materials with known and controlled speciation of active component. Many catalysts investigated in the ODH reaction are based on the vanadium oxides as the main component [7–32]. Bulky vanadium pentoxide, in fact, is not a good catalytic system for the selective oxidation of alkanes, but spreading the oxide on the quasi-inert matrix leads to formation of the centers with peculiar chemical–physical features and reactivity. The vanadium oxides supported on surface of micro- or mesoporous materials are of a great interest of scientific community due to the ability to combine unique textural and acid–base properties of support materials with the redox properties of vanadium oxide species which opens the possibility to activate alkanes at relatively low temperatures.

Vanadium oxide supported on the surface of silica is more selective in propane ODH (C3-ODH) than those prepared using the alumina or titania as a supports. Mesoporous siliceous materials provide sufficiently high surface area for the successful spreading and isolation of anchored vanadium species. VO_x-containing mesoporous silica materials, such as MCM-41 [20,23,26,33–35], SBA-15 [21,32–34,36] and HMS [15,23,32,33], have shown promising catalytic performance in the C3-ODH. In many cases, site isolation has been achieved by the simple deposition of the active phase using wet impregnation [37–40]. However, impregnation methods very often resulted in materials with broader distribution of VO_x species including also VO_x units with a lower degree of dispersion or bulk oxide. Therefore, more sophisticated post-synthesis methods, such as grafting/ion-exchange method [41–44], molecular designed dispersion [45,46] and chemical vapor deposition [47,48], were utilized for synthesis of VO_x based catalysts. These advanced post-synthesis methods usually lead to better dispersion of vanadium. On the other hand, several operating steps and

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* Corresponding author. Tel.: +420 466 037 511; fax: +420 466 037 068.
E-mail address: Roman.Bulanek@upce.cz (R. Bulánek).

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expensive compounds are required especially for grafting and molecular dispersion methods. An alternative route for the incorporation of vanadium species on the silica surface is the direct hydrothermal synthesis in which the required amounts of proper metal salts (NH_4VO_3, vanadyl sulfate, vanadyl acetylacetonate) is introduced to the synthesis gel [49–54]. The one-pot synthesis method results in materials with fine dispersion of vanadium having smaller extent of oligomerization and negligible amount of V_2O_5 domains. Despite a huge progress in the development of advanced method for one-pot synthesis of functionalized mesoporous silicas [55–57], approaches based on post-synthesis functionalization remain still popular due to the fact that the separation of the silica synthesis and the functionalization steps allows independent and more straightforward control of pore periodicity and particle size and morphology.

In this study, we report a simple one-pot synthesis method for preparation of VO_x-HMS catalysts with a wide range of vanadium content (1–14 wt.%) leading to samples without microcrystalline V_2O_5 oxide up to vanadium surface density 3.32 V/nm^2. Directly synthesized catalysts were compared as for catalytic behavior and physico-chemical characteristics to catalysts prepared by conventional wet impregnation method. It was shown that the catalysts prepared by one-pot synthesis exhibit superior catalytic performance. Propene productivity reached over our directly synthesized catalysts was up to 3 times higher than productivity of impregnated samples under the same conditions. In addition, our data indicate that both monomeric VO_4 vanadyl species and tetrahedrally coordinated oligomeric VO_x species containing V—O—V bonds act as active sites responsible for activity and selectivity.

2. Experimental

2.1. Preparation of catalysts

Investigated vanadium catalysts were prepared by the wet impregnation and the direct synthesis method. Hexagonal mesoporous silica (HMS) used for preparation of impregnated catalysts was synthesized according to the procedure reported by Tanev and Pinnavaia [58]. Briefly, HMS was prepared by dissolving 13.6 g dodecylamine (DDA, Aldrich) in the mixture that contains 225 cm^3 of ethanol and 200 cm^3 of double-distilled H_2O. After stirring for 20 min, 56 cm^3 of tetraethyl orthosilicate (TEOS, Aldrich) was added dropwise and intensively stirred. The reaction was performed at 25 °C for 18 h under stirring. The solid product was filtered and then repeatedly suspended in 500 cm^3 of EtOH and stirred at 25 °C for 1 h in order to remove major part of DDA from obtained solid. Finally, the solid was calcined in air flow at 450 °C for 20 h (with heating rate 1 °C min^{-1}). Vanadium oxo-complexes were doped onto silica support by wet impregnation by EtOH/H_2O solution of vanadyl acetylacetonate. Impregnated samples were dried overnight at 120 °C in air and then calcined at 600 °C for 8 h (with heating rate 5 °C min^{-1}). The vanadium loading of final catalysts varied in the range 1.0–15.7 wt.% of vanadium in the final catalysts.

Directly synthesized VO_x-HMS catalysts were prepared by the procedure analogous to the pure HMS synthesis. The porous vanadosilicates were prepared at 25 °C by employing tetraethyl orthosilicate as a silicon source, vanadyl acetylacetonate as a vanadium source and dodecylamine as a structure directing agent. 4.5 g of dodecylamine were dissolved in the mixture of 75 cm^3 of ethanolic solution of vanadyl acetylacetonate of appropriate concentration and 66 cm^3 of double-distilled H_2O. Then, tetraethyl orthosilicate (19 cm^3) was added dropwise to this solution and stirred at 25 °C for 18 h. The solid product was filtered and then repeatedly suspended in 150 cm^3 of ethanol and stirred at 25 °C for 1 h in order to remove DDA from pores of solid. Finally, the solid was calcined in air flow at 600 °C for 8 h (with heating rate 1 °C min^{-1}).

The investigated samples were denoted as i-S-*x* and s-S-*x* for impregnated and synthesized samples, respectively, where *x* is the vanadium content in weight percentage.

2.2. Catalysts characterization

The chemical composition of all investigated samples was determined by X-ray fluorescence spectroscopy (bench-top vacuum wavelength dispersive X-ray spectrometer Spectroscan V, Spectron, Russia). Homogeneous mixture of catalyst and boric acid was pressed into the pellets of 12 mm diameter with the average thickness 2 mm. All pellets were continuously rotated during analysis for removing their potential heterogeneity. Results of the elemental analysis are summarized in Table 1.

Structure and crystallinity of catalysts were probed by X-ray diffraction (D8-Advance diffractometer, Bruker AXE, Germany) using Cu Kα radiation ($\lambda = 1.5406$ Å) and scanning electron microscopy (SEM) using JSM-5500LV microscope (JEOL, Japan).

Specific surface area and texture of investigated samples was measured by means of nitrogen adsorption/desorption at temperature of liquid nitrogen using the ASAP 2010 equipment (Micromeritics, USA). Prior to the adsorption isotherm measurement, the samples were degassed overnight at 300 °C under vacuum. The BET surface area was evaluated using adsorption data in a relative pressure range from 0.05 to 0.25 (Table 1). The mesopore volume (V_{ME}) and mesopore distribution of silica materials were calculated using BJH algorithm (Table 1) calibrated to accurately determine the pore diameter and volume.

Redox behavior of VO_x surface species was investigated using of the temperature programmed reduction by hydrogen (H_2-TPR) using the AutoChem 2920 (Micromeritics, USA). A 150 mg sample in a quartz U-tube microreactor was oxidized in oxygen flow at 500 °C (2 h) prior to the TPR measurement. The reduction was carried out from 25 °C to 900 °C with a temperature gradient of 10 °C min^{-1} in the flow of reducting gas (5 vol.% H_2 in Ar). The changes in hydrogen concentration were monitored by the TCD detector. Simultaneously, hydrogen consumption and water formation were also detected on a quadrupole mass spectrometer OmniStar^{TM} GDS 300 (Pfeiffer vacuum, Germany) by means of mass fractions (2, 18, 28, 32 and 44 amu) monitoring every 3 s in all tests.

Distribution of vanadium species was investigated by UV–vis diffuse reflectance spectroscopy. DR-UV–vis spectra of dehydrated granulated (0.25–0.50 mm) materials were recorded using GBS CINTRA 303 spectrometer (GBC Scientific Equipment Pty Ltd., Australia) equipped with a diffuse reflectance attachment with a Spectralon-coated integrating sphere and using a Spectralon-coated disc as a reference. The absorption intensity was expressed using the Schuster–Kubelka–Munk equation, $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. Dehydration of vanadium-based catalysts was carried out in the static atmosphere of oxygen in two steps: 120 °C for 30 min and 450 °C for 60 min with heating rates 10 °C min^{-1}. The samples were then cooled down to 250 °C and evacuated for 30 min. This procedure guaranteed that the vanadium species did not coordinate water molecules. After dehydration, the samples were cooled down to ambient temperature and transferred under vacuum into the optical cell of 5 mm thickness and sealed. Dehydration of catalyst was independently checked on selected samples by UV–vis–NIR spectroscopy monitoring vibrations of OH overtones (not shown for sake of brevity). Obtained spectra were transformed to the dependencies $(F(R_\infty)\cdot h\nu)^2$ against $h\nu$ and ε_0 were determined from obtained plots of Tauc's law [59] which can be expressed as: $(F(R_\infty)\cdot h\nu)^2$ is proportional to $(h\nu - \varepsilon_0)$, where the ε_0 is the energy