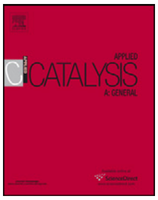
Applied Catalysis A: General 415–416 (2012) 29–39

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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



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

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ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form
29 November 2011
Accepted 30 November 2011
Available online 8 December 2011

Keywords:
Vanadium
ODH
Propane
Propene
Mesoporous silica
TPR
UV–vis
HMS

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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doi:10.1016/j.apcata.2011.11.033