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Propane oxidative dehydrogenation over VO_x/SBA-15 catalysts

Gheorghita Mitran[a], Rawaz Ahmed[b,1], Emmanuel Iro[b], Saeed Hajimirzaee[b], Simon Hodgson[b], Adriana Urdă[a,*], Maria Olea[b], Ioan-Cezar Marcu[a,*]

[a] *Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018 Bucharest, Romania*
[b] *School of Science and Engineering, Teesside University, Middlesbrough, United Kingdom*

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ABSTRACT

VO_x/SBA-15 catalysts with five different vanadium loadings were prepared by a modified wet impregnation method, characterized using N_2 adsorption, XRD, EDX, SEM, Raman and UV–vis spectroscopies and H_2-TPR techniques, and tested in the oxidative dehydrogenation of propane in the temperature range 450–600 °C. For all the catalysts the propane conversion increases with both reaction temperature and vanadium loading, while the selectivity for propene decreases mainly to the benefit of carbon oxides. Several types of VO_x species coexist on the catalyst surface, with monomeric and low-polymerized ones leading mainly to propene, while V_2O_5 crystallites at high vanadium loadings producing more carbon oxides. Propene was determined to be the only primary product irrespective of the vanadium content.

1. Introduction

The increasing demand in unsaturated hydrocarbons for the manufacturing of polymers, synthetic fibers, detergents, elastomers and synthetic fuels, has triggered the development of inexpensive and environmentally friendly ways of their production. The lower price of alkanes compared to the corresponding alkenes makes their use as feedstock in the chemical and petrochemical industry very attractive [1–3]. However, the current alkanes conversion technology, based on the dehydrogenation process, has several disadvantages, such as high endothermicity, unfavorable equilibrium shift and difficult control of cracking side reactions at high temperatures, which contribute to the rapid coking of the catalyst [1,3,4]. Therefore, the alternative conversion route consisting in the oxidative dehydrogenation (ODH) process becomes promising from engineering and economic points of view by overcoming all these drawbacks [1,5–7]. The main problem remains avoiding side reactions leading to oxygen-containing organic molecules and carbon oxides, which severely limit the selectivity to dehydrogenation products [1,8,9]. Early attempts to use other oxidants (i.e. iodine) were abandoned due to corrosion and environmental problems posed by the oxidant [1]. Recently, N_2O was also used as oxidation agent in ODH reactions with interesting results [10,11].

Many catalysts have been tested for the ODH reaction, but supported vanadia and molybdena proved to be the most active and selective ones [12]. In both cases, the most selective catalysts contain well-dispersed vanadium or molybdenum species onto the support surface, at near monolayer coverage, which is about 7.5 V nm^{-2} for polyvanadate [13] and about 4.8 Mo nm^{-2} for polymolybdate; however, vanadia has higher ODH activity than molybdena at equivalent dispersion [6]. Notably, much lower values corresponding to the monolayer coverage were more recently proposed for catalysts supported on silica (0.7 V nm^{-2}) and explained by the lower density and reactivity of silica surface hydroxyl groups [8]. Vanadium oxide catalysts supported on various oxides, such as SiO_2, Al_2O_3, TiO_2, Nb_2O_5, MgO, La_2O_3, Sm_2O_3 and Bi_2O_3, to mention some of them, have been extensively studied [1,7,14,15]. Their catalytic performance in the ODH of alkanes depends on the nature of the support (which, in turn, is partly responsible for the vanadium reducibility and dispersion), the vanadium loading and the preparation conditions, which influence the nature and structure of the VO_x surface species [5,15]. Moreover, the acid-base character of the support affects the catalytic performance [15]. It has been found that in the ODH of propane the most selective catalysts were obtained with vanadium supported on basic, rather than on acidic metal oxides. It has also been found that VO_x species with V in octahedral and tetrahedral positions are the active ones, the tetrahedral being less active but more selec-

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* Corresponding authors.
E-mail addresses: adriana.urda@chimie.unibuc.ro (A. Urdă), ioancezar.marcu@chimie.unibuc.ro (I.-C. Marcu).

[1] Present address: Kurdistan Institution for Strategic Studies and Scientific Research (KISSR), Qirga, Slemani, As Sulaymaniyah, Iraq.

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tive. The higher the concentration of VO^{2+} and V_2O_5 species the lower is the selectivity to propene [16]. The presence of polymerized vanadium species and bulk V_2O_5 is detrimental to the activity of the catalyst as well, as less vanadium atoms are accessible to the propane molecules. In order to minimize the formation of V_2O_5 crystallites responsible for the formation of CO_x, oxide supports with high surface area and lower reducibility than vanadia are used [6,7,17]. The support plays an important role in the dispersion of the active phase, on the accessibility, reactivity and acidity of the active sites, and also on the mass/heat transfer phenomena [18]. Combining the textural and acid-base properties of the support with the redox properties of the vanadia species makes it easier to activate alkanes at lower temperatures [19].

Silica-supported vanadia catalysts were reported to be active in propane ODH [5] and, in order to increase the propene yields, mesoporous siliceous materials such as MCM-41, MCM-48, mesocellular foams (MCF) and SBA-15 were used as supports [5,20,21]. SBA-15 is a mesoporous silica, characterized by large surface area and formed by a hexagonal array of uniform tubular channels, with tunable pore diameters in the range of 5–30 nm and very narrow pore-size distribution [22,23]. It has been used as support for catalysts in the ODH of butanes [24,25], ethane [26], ethylbenzene [11], as well as for methanol oxidation [23,27].

Propane ODH on vanadia supported on mesoporous SBA-15 has been studied by several groups [17,22]. However, since both silica and vanadia possess acidic character, it is very challenging to prepare catalysts with high dispersion at high loadings. Therefore, the preparation method and conditions should be carefully chosen. Some of the preparation methods used so far are: alcoholic impregnation [20,22], wet impregnation [17,24,28], mechanical mixing [22], direct synthesis [18,29], adsorption [22] and grafting-ion exchange [27,30,31]. Although superior performances of the mesoporous VO_x/SBA-15 catalysts have already been reported [22], a fundamental understanding of their behavior towards the propane ODH remains to be accomplished.

The aim of this paper is to investigate further the catalytic activity of the SBA-15-supported vanadia catalysts and to gain a deeper insight into their structure-activity relationship. In order to accomplish these goals, a series of VO_x/SBA-15 catalysts, with vanadium loadings between 6.5 and 11 wt%, were prepared using an improved impregnation method and their detailed characterization by N_2-adsorption, SEM/EDX, XRD, H_2-TPR, Raman and UV–vis spectroscopies as well as their catalytic performance in the oxidative dehydrogenation of propane have been performed.

2. Experimental

2.1. Support preparation

The general experimental procedure followed in the preparation of SBA-15 mesoporous silica was described in detail by Zhao et al. [32]. However, this procedure was modified and the preparation conditions, such as the amount of P123, type of acid and aging time, were optimized through experiments. The optimized procedure is described below.

4 g of Pluronic 123 triblock copolymer (EO20-PO70-EO20, P123, Sigma-Aldrich) was dissolved into 120 g of deionised (DI) water at 40 °C, under vigorous stirring for 6 h. Then 20 ml of 2 M HCl (Fisher Scientific) was added to the clear solution and after 10 min, 9.25 g of TEOS (Tetraethylorthosilicate, Sigma-Aldrich) was introduced dropwise, the solution being kept under vigorous stirring at 40 °C for 20 h. A white precipitate was formed which was kept in an oil bath at 95 °C for 24 h, without stirring, then filtered, washed with 600 ml of deionised water and dried at 60 °C for 24 h. The white powder was then calcined at 550 °C, under steady-state conditions, for 6 h, at a heating rate of 10 °C min^{-1}. After calcination, the sample was cooled down to 60 °C at a cooling rate of 10 °C min^{-1} and placed in a round bottom flask with a short condenser inside to be re-hydrated by using 50 g of DI water. The suspension was then placed in an oil bath at 105 °C and left boiling under a gentle stirring. After 2 h, the suspension was filtered and 2 g of SBA-15 sample were collected by filtration and dried a 120 °C for 6 h.

2.2. Catalyst preparation

Five SBA-15-supported vanadia samples were prepared by wet impregnation. A solution of ammonium vanadate, NH_4VO_3 (Sigma-Aldrich), was contacted with the SBA-15 support, under stirring, at 55–60 °C for 2 h, to achieve a final V content of 6.5–11.0 wt%. The solid product was recovered by filtering and then dried in vacuum, at 100 °C, for 1 h, followed by calcination in air at 600 °C, for 5 h, at a heating rate of 5 °C min^{-1}. The impregnated samples were labelled as *x*V, where *x* denotes the wt% of V.

2.3. Catalysts characterization

The textural characterization was performed using the nitrogen adsorption/desorption method, with a Micromeritics ASAP 2010 automatic equipment. The surface areas were calculated using the BET method in the relative pressure, P/P_0, region 0.065–0.2, while the pore sizes were determined by the BJH method from the nitrogen desorption branch. Prior to nitrogen adsorption, the samples were degassed at 150 °C for 10 h.

Scanning Electron Microscopy (SEM) accompanied by X-ray energy dispersion analysis (EDX) was used to monitor the morphology and surface composition of the catalysts samples. SEM/EDX examination was performed using a Hitachi S-4500 field emission microscope with a Quartz PCI XOne SSD X-ray analyser.

To obtain information on both, the mesoporous structure and the crystalline structure of the SBA-15-supported vanadia catalysts, small- and wide-angle X-ray diffraction (XRD) patterns were recorded on a Bruker D8 (25 kV, 20 mA) powder X-ray diffractometer, using Cu Kα radiation ($\lambda = 0.15406$ nm), a tube voltage of 40 kV, and a current of 20 mA. The data were collected from 0.5 to 4° (2θ) with a resolution step size of 0.01° (small-angle XRD patterns) and from 10 to 70° (2θ) with a resolution step size of 0.02° (conventional wide-angle XRD patterns).

The type of V species formed on the surface of the SBA-15 was studied with Raman spectroscopy. The Raman spectra were recorded with a Raman Microscope Spectrometer Horiba Jobin Yvon – Labram HR UV–vis-NIR, between 100 and 1200 cm^{-1}, using a 633 nm wavelength for excitation. Before recording the spectra, the spectrometer was calibrated using the Raman band at 520 cm^{-1} of a standard SiO_2 sample.

The UV–VIS spectra were recorded using a UV3600 UV–vis spectrophotometer with Shimadzu ISR-3100 integrating sphere attachment having an angle of incident light of 0–8°, two light sources: D2 (deuterium) lamp for the ultraviolet range and WI (halogen) lamp for the visible range and a PMT (photomultiplier tube) detector. The spectra were recorded in the range of 190–800 nm (the switching wavelength of the lamps is between 282 nm and 393 nm) with a wavelength step of 2 nm, having the slit width of 8 nm. The spectra were measured using samples diluted with extra pure barium sulfate (Nacalai Tesque).

The reducibility of the catalysts was studied by temperature programmed reduction under hydrogen (H_2-TPR). Experiments were performed using a CATLAB microreactor – MS system (Hiden Analytical, UK) under a flow of 5% H_2/Ar mixture through the CATLAB's packed micro-reactor containing about 35 mg of sample, which was heated at a constant rate of 20 °C min^{-1} up to 850 °C. The system

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