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# Structure of alumina supported vanadia catalysts for oxidative dehydrogenation of propane prepared by flame spray pyrolysis

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ABSTRACT

A series of five vanadia on alumina catalysts for oxidative dehydrogenation of propane to propene were synthesized by flame spray pyrolysis (FSP) using vanadium(III)acetylacetonate and aluminium(III)acetylacetonate dissolved in toluene as precursors. The vanadium loading was 2, 3, 5, 7.5 and 10 wt.%. The catalysts were subsequently characterized by BET surface area, X-ray diffraction (XRD), Raman, UV–vis diffuse reflectance and X-ray absorption spectroscopy (XAS) as well as measurement of the catalytic performance. The catalysts had specific surface areas from 143 to 169 $m^2/g$ corresponding to average particles diameters from 9.0 to 10.9 nm and apparent vanadia surface densities from 1.4 to 8.4 $VO_x/nm^2$. The only crystalline phase detected by XRD was $\gamma$-$Al_2O_3$, except at 10 wt.% vanadium where traces of crystalline vanadia were observed. Raman spectroscopy showed vanadia monomers at 2 and 3 wt.% V (1.4 and 2.1 $VO_x/nm^2$), a mixture of vanadia oligomers and monomers at 5 wt.% V (3.6 $VO_x/nm^2$) and mainly oligomers at 7.5 and 10 wt.% V (6.0 and 8.4 $VO_x/nm^2$). Diffuse reflectance UV–vis and extended X-ray absorption fine structure (EXAFS) spectroscopy measurements supported the results of Raman spectroscopy. In situ X-ray absorption near edge structure (XANES) spectroscopy showed that the vanadia can be reduced when operating at low oxygen concentrations. The catalyst performance was determined in fixed bed reactors with an inlet gas composition of $C_3H_8/O_2/N_2 = 5/25/70$. The main products were propene, CO and $CO_2$, with traces of ethene and acrolein. Comparing propene selectivity as function of propane conversion the most selective catalysts were the 2 and 3 wt.% V samples, which contained mostly vanadia monomers according to Raman spectroscopy. The best propene yield of 12% was obtained with the 2 wt.% vanadium catalyst while the best space time yield of 0.78 $g_{propene}/(g_{cat}\cdot h)$ at 488 °C was obtained with the 3 wt.% V catalyst.

## 1. Introduction

Upgrading $C_2$ to $C_4$ alkanes to the corresponding alkenes may become interesting processes to meet future demands for light alkenes [1], particularly for propene [2]. Light alkenes are mainly produced by fluid catalytic cracking (FCC), where they are byproducts in the upgrading of heavy oil fractions, and by steam cracking where the reaction conditions can be optimized to yield mainly ethene or mixtures of propene and butenes [2]. Processes for catalytic dehydrogenation of propane to propene have also been developed, employing chromium or platinum based catalysts [3,4]. The major drawbacks of these three processes are the high energy consumption due to the endothermic reactions and coking of the catalysts and reactors, leading to deactivation and lower yields [2,3]. To overcome this problem, some processes use multiple swing reactors where some are on-stream, while others are being regenerated [4].

Catalytic oxidative dehydrogenation of propane (ODP) is another process which could be employed for dedicated production of propene. This reaction is exothermic and the oxidizing reaction conditions eliminate the problem of coking, as long as the oxidant is not completely consumed [5]. The major drawback of ODP is lower selectivity, since propane, as well as the propene product, are easily combusted to CO and $CO_2$ [6]. So far no catalyst with sufficient selectivity for industrial production of propene has been reported in the literature, despite high research and development activities [1].

Flame spray pyrolysis (FSP) is a novel method for fast and continuous production of nanoparticles [7,8]. Combustible precursors dissolved in organic solvents are sprayed with high velocity oxygen to create a spray of micrometer sized droplets [9]. The spray is ignited by a premixed methane-oxygen flame in a concentric ring

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surrounding the spray of precursor solution, which is the main fuel for the flame. Combustion of the precursor droplets results in atomically dispersed vapors which nucleate to form nanoparticles from the gas phase. The particles grow and sinter until reaching cooler parts of the flame, where they form aggregates and agglomerates. The combustion enthalpy must be high enough for quick evaporation of the precursor droplets. Otherwise particle formation may occur in the liquid phase. This results in micrometer-sized solid, hollow or shell-like particles [7].

When preparing supported catalysts by FSP the precursors for the support material and the active phase(s) are mixed in one precursor solution [10]. The support material must first nucleate in order for the active phase to condensate on the surface of the support nanoparticles [11]. For vanadia this is the case with typical oxide supports like $SiO_2$, $Al_2O_3$ and $TiO_2$. Thus supported vanadia species, rather than separated or mixed crystalline phases of the support and vanadia, are the products of FSP and vapor flame synthesis [12–15].

Alumina supported vanadia catalysts have been prepared by FSP by Rossetti and co-workers [16]. The specific surface areas obtained in their study ranged from 18 to 27 $m^2/g$, approximately a factor 5–10 lower than what is typical for alumina supported catalysts prepared by FSP [17]. SEM images reported by Rossetti et al. also showed a very broad particle size distribution. This may be due to the use of aluminum nitrate as precursor, which contains large amounts of water, so that the combustion enthalpy of the precursor solution may have been too low for fast evaporation of the precursor droplets. Another reason could be the low dispersion gas pressure drop across the nozzle [18], leading to larger precursor droplets which evaporate slowly. Consequently crystalline $V_2O_5$ and $AlVO_4$ were produced rather than supported vanadia species.

This study aims at preparing vanadia on high surface area alumina catalysts and gaining insights to the structure–activity–selectivity relationship of oxidative dehydrogenation of propane as function of vanadia loading. For this purpose the corresponding acetylacetonates dissolved in the high combustion enthalpy solvent toluene were used as precursors during flame synthesis.

## 2. Experimental

### 2.1. Catalyst preparation

Aluminium(III)acetylacetonate and vanadium(III)acetylacetonate (used as received from Sigma Aldrich) were dissolved in anhydrous toluene to a total metal concentration of 0.4 M in ratios for preparation of 2, 3, 5, 7.5 and 10 wt.% V on alumina assuming the products are $V_2O_5$ and $Al_2O_3$ (see Table 1). After stirring and gentle heating to about 50 °C clear green–brown solutions were obtained. FSP synthesis was performed on a setup described in detail in ref. [19]. The precursor solutions were sprayed at 5 ml/min with 5 Nl/min $O_2$ as dispersion gas at 1.8 bar pressure drop. The supporting flame was maintained at 1 Nl/min $CH_4$ and 3 Nl/min $O_2$. The product particles were collected on Whatman GF6 glass fiber filters by means of a vacuum pump (Busch).

### 2.2. Catalyst characterization

The specific surface area (SSA) was measured on the as-prepared FSP powder, after degassing at 170 °C in a flow of dry nitrogen, by nitrogen adsorption at its boiling point (Quantachrome $iQ_2$) using multipoint BET theory with six points in the $p/p_0 = 0.05–0.25$ range. The BET average particle diameter assuming spherical particles was calculated as $d_p = 6/(\text{SSA}\cdot\rho)$, where $\rho$ is the $Al_2O_3$ and $V_2O_5$ wt.% weighted average density. The apparent $VO_x/m^2$ surface density was calculated from the vanadium loading and the SSA.

Powder X-ray diffraction (XRD) patterns was recorded on as-prepared powders using rotating sample holders, a rotating copper anode X-ray source, nickel filter and automatic anti-scatter and divergence slits with a scan speed of 0.0102°/s (PANalytical X'Pert PRO).

Laser Raman spectroscopy was performed with a Horiba Jobin Yvon spectrometer (LabRAM HR) attached to an Olympus microscope. An Argon ion laser, tuned to the 514.5 nm line was used for excitation and the Raman scattered light was collected from 100 to 1100 $cm^{-1}$ with a 1800 gratings/mm monochromator, 120 s integration time and 10 repeats to reduce the signal-to-noise ratio. The catalysts were pressed and crushed to 150–300 μm particles and placed in a modified fluidized bed in situ cell (Linkham CCR1000). The catalysts were dehydrated in a flow of dry air at 550 °C and cooled to room temperature in flowing air before measuring the Raman spectra.

UV–vis diffuse reflectance spectra (Varian Cary 300 Bio) were recorded on the as-prepared powders using an integrating sphere (Labsphere DRA-CA-30I) with Spectralon as reference. Spectra were analyzed using the Kubelka–Munk theory, $F(R_\infty) = (1 - R_\infty)^2/(2R_\infty)$ where $R_\infty$ is the reflectance of an infinite layer relative to the reference. The absorption edge energy was determined as the $h\nu$-axis intercept of a straight line fitted to the low energy rise of a plot of $(F(R_\infty) \times h\nu)^2$ as function of $h\nu$, where $h\nu$ is the photon energy in eV. For the 5, 7.5 and 10 wt.% V catalysts two absorption edges were observed and a straight line was fitted to each section on the $(F(R_\infty) \times h\nu)^2$ plot.

X-ray absorption spectroscopy was performed at the ANKA-XAS beamline at the ANKA synchrotron radiation source (Karlsruhe, Germany). The 10 wt.% V sample was diluted with cellulose powder and pressed as a pellet for ex situ measurement in transmission mode. The as-prepared FSP powder (3–5 mg) of the 3, 5 and 7.5 wt.% samples were placed in an in situ transmission cell with graphite windows. Extended X-ray absorption fine structure (EXAFS) spectra of the as-prepared catalysts were recorded of all three samples. The 2 wt.% sample was loaded in a Kapton capillary to minimize background absorption for ex situ measurement. The ex situ EXAFS spectra were recorded from $E = 5.315$ to 6.445 keV in 385 steps with 1 s integration time per step at low energy and progressively longer integration time up to 4 s at the highest energy. Fourier transformations of the EXAFS spectra were performed with $k^2$-weighting in the $k = 2–11$ Å$^{-1}$ range. The 3, 5 and 7.5 wt.% V catalysts were investigated in situ with simultaneous catalytic activity measurements and XANES when loaded in the transmission cell (7.5 wt.% catalyst) or in a quartz capillary above a hot air blower [20]. The catalysts were first oxidized at 550 °C in 10% $O_2$/He. Then the temperature was reduced to 400 °C and oxidative dehydrogenation of propane was performed using two reaction gas mixtures (2.5% $C_3H_8$, 6.7% $O_2$ or 5.0% $C_3H_8$, 3.3% $O_2$ and He balance) by ramping the temperature from 400 to 500 °C at 1 °C/min. After re-oxidation in 10% $O_2$/He at 500 °C, in situ TPR (5% $H_2$/He) with a temperature ramp of 5 °C/min from room temperature to 600 °C was performed. The 3 and 5 wt.% catalysts were only investigated in the richer gas mixture at slightly lower temperatures due to differences between the temperature of the capillary and the hot air blower. The total gas flow was 30 Nml/min in all experiments. XANES spectra were recorded from $E = 5.400$ to 6.000 keV in 1628 steps with 0.075 s integration time. This resulted in approximately 6 min for each spectrum including the time for initialization and double crystal monochromator movement. After normalization of the spectra the absorption edge energy $E_0$ values were determined as a set fraction of the white-line intensity (0.80). On-line gas analysis was performed by means of both mass spectrometry (MS, Pfeiffer ThermoStar) and Fourier transform infrared (FTIR, MKS instruments) based gas analyzers.