Characterisation and catalytic testing of VO_x/Al_2O_3 catalysts for microstructured reactors

Oliver Schwarz [a], Benjamin Frank [a], Christian Hess [b], Reinhard Schomäcker [a,*]

[a] *Department of Chemistry, Technical University of Berlin, Straße des 17. Juni 124-128, D-10623 Berlin, Germany*
[b] *Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany*

Abstract

With regard to the application in a microstructured reactor, a special VO_x/Al_2O_3 catalyst powder (3 μm) was prepared and characterised by BET, XRD, UV/Vis DRS, and Raman spectroscopy. The higher the vanadium content, the higher the degree of polymerisation of the vanadium species on the support surface and the lower the BET surface area. Pelletised powders were tested in conventional tubular reactors for their catalytic performance in the oxidative dehydrogenation of propane. Their activity increases with vanadia loading, whereas selectivity towards propene decreases at iso-conversion. Catalytic benchmarking was performed to choose a reasonable catalyst for further investigations in a microreactor.
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1. Introduction

Lower olefins are conventionally produced from non-oxidative, high-temperature cracking processes which are energy-extensive and commonly suffer from catalyst deactivation by coking. Additionally, the ratio of desired products to by-products is difficult to influence by a variation of process parameters. One of the proposed alternatives is the oxidative dehydrogenation of alkanes at relatively low temperatures such as 673–873 K [1]. Especially, the production of propene has been subject to research for several years since the demand for propene grows at a constant rate [2–4]. One of the main drawbacks of the oxidative dehydrogenation of propane (ODP) according to Eq. (1) states the low selectivity towards propene. This is due to its consecutive combustion to carbon oxides according to Eq. (2).

$$C_3H_8 + 0.5O_2 \rightarrow C_3H_6 + H_2O \tag{1}$$

$$C_3H_6 + (4.5 - 0.5x)O_2 \rightarrow xCO + (3 - x)CO_2 + 3H_2O \tag{2}$$

This simplified reaction scheme was found to be appropriate for the description of the ODP over a low loaded (apparent surface density of 1.6 VO_x nm^{-2}) VO_x/γ-Al_2O_3 catalyst [5]. Activity and selectivity in the oxidative dehydrogenation sensitively depend on the dispersion and structure of the vanadia species on the support material. Consequently, a detailed characterisation of the tested catalyst is necessary for optimisation of the catalytic material [6,7]. Selectivity behaviour of VO_x/Al_2O_3 catalysts in the ODP reported in literature differs remarkably. Kondratenko and Baerns noted that selectivity towards propene increases with increasing vanadia surface coverage at low vanadia contents [8], whereas Argyle et al. observed a reverse tendency [9]. This is most likely due to different starting materials, preparation methods and experimental set-ups.

In addition to improved catalyst understanding and performance, also new reactor concepts might help to make the oxidative dehydrogenation economically reasonable.

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* Corresponding author. Tel.: +49 30 314 24973; fax: +49 30 314 21595.
  E-mail address: schomaecker@tu-berlin.de (R. Schomäcker).

Microreaction technology offers some outstanding advantages in comparison to conventional reactor systems such as isothermal operation conditions, uniform residence time distributions and the absence of mass transfer limitations because of thin catalyst coatings [10–12]. These advantages seem to be very useful for improving the overall performance of the ODP since it is a very fast and strongly exothermic reaction that suffers from heat and mass transfer limitations in conventional reactor geometries [5]. The relatively small primary particle size of 3 μm allows for the application of this material in microreactors, which was already successfully tested for several samples loaded with different vanadium amounts.

2. Experimental

2.1. Catalyst preparation

VO_x/Al_2O_3 catalyst samples were prepared by the incipient wetness impregnation method. With regard to the suitability for coating microstructures with thin catalytically active layers, a γ-Al_2O_3 powder (Alfa Aesar) with a mean particle diameter of 3 μm was chosen as support material. The small particle size requires a specialised preparation method. Therefore, the γ-Al_2O_3 powder was physically mixed with vanadyl acetylacetonate (Fluka, >97%). The ratio of these components was varied to obtain catalytic materials with different vanadium content. This mixture was then suspended in methanol aided by ultrasound (methanol being the only solvent readily supporting full dispersion of Al_2O_3 agglomerates formed from primary particles). Since simple drying methods did not yield a uniform dispersion of the precursor substance on the support material, methanol was removed by rotary evaporation. Afterwards, the obtained catalyst was calcined at 773 K for 5 h. Drying and calcination resulted in the formation of relatively large agglomerates. For catalytic testing, these were crushed and sieved into different fractions.

2.2. Catalyst characterisation

The specific BET surface areas of the γ-Al_2O_3 powder and the prepared catalysts were measured using nitrogen adsorption at 77 K with a micromeritics Gemini III 2375 Surface Area Analyzer.

In situ UV/Vis diffuse reflectance spectroscopy (UV/Vis DRS) was performed using an AVASPEC fibre optical spectrometer (Avantes) equipped with a DH-2000 deuterium–halogen light source and a CCD array detector. $BaSO_4$ was used as a white reference material. Spectra were recorded at 773 K in an O_2:Ne = 20:80 flow $(40\ ml_n\ min^{-1})$.

For X-ray diffraction (XRD) experiments, a Siemens D5005 diffractometer with a Cu K_α radiation source $(\lambda = 0.154\ nm)$ was used. The analysis was run from 15 to 50° (2θ) to detect crystalline V_2O_5 structures on the support.

Raman experiments were performed using a fibre probe, which was inserted into an *in situ* Raman cell. The powder samples were placed in a stainless steel sample holder with a 0.6 mm deep rectangular well covering an area of $(12 \times 8)\ mm^2$. Prior to experiments, the samples were dehydrated by treatment in 20% O_2:He $(50\ ml_n\ min^{-1})$ at 573 K for 60 min and subsequently cooled to room temperature. Raman spectra were recorded using 514 nm laser excitation (5 mW) at 5 cm^{-1} spectral resolution (Kaiser Optical). Sampling times were typically 30 min.

2.3. Catalytic tests

ODP experiments were carried out in a packed bed tubular reactor made of quartz glass with plug flow hydrodynamics. The catalyst with a particle diameter of 100–300 μm was chosen for catalytic testing. For better heat transfer, all catalyst samples were diluted with 1.9 g quartz sand resulting in similar lengths of the packed bed. Blind testing of empty reactors, quartz sand and pure γ-Al_2O_3 did not lead to detectable conversions up to 773 K. Reaction products were analysed by a gas chromatograph (Satochrom) equipped with a flame ionisation detector and a thermal conductivity detector as well as a fused silica capillary column and a molecular sieve column. The composition of the inlet flow was C_3H_8:O_2:N_2 = 2:1:4, using synthetic air as oxygen source. Experiments were carried out in a temperature range from 673 to 798 K with catalyst masses from 7.6 to 199.7 mg and total volume flows from 30 to 240 $ml_n\ min^{-1}$. As reaction products, C_3H_6, CO, CO_2, and H_2O were detected. Conversion of propane and selectivity towards propene were calculated according to Eqs. (3) and (4).

$$X = (p_{C_3H_{8,0}} - p_{C_3H_8})/p_{C_3H_{8,0}} \tag{3}$$
$$S = p_{C_3H_6}/(p_{C_3H_{8,0}} - p_{C_3H_8}) \tag{4}$$

3. Results and discussion

As a first step in the process design for the oxidative dehydrogenation of propane in microstructured reactors, VO_x/Al_2O_3 powder catalyst samples with varying vanadium content (1.4, 3.4, 5.3, and 7.8 wt% V) were prepared and thoroughly characterised. The adjusted vanadia concentrations resulted in apparent surface densities of 2.1, 5.2, 8.3, and 12.5 $VO_x\ nm^{-2}$, respectively.

The BET surface area of the investigated catalysts as a function of their vanadium content is shown in Fig. 1a. The pure γ-Al_2O_3 support material provides a surface area of 80 $m^2\ g^{-1}$. With increasing vanadium content the catalyst suffers a loss of surface area, probably due to clogging of micropores with vanadia.

To get insight into the dispersion of the vanadia species on the catalyst surface, UV/Vis, XRD, and Raman experiments were performed. UV/Vis spectra of the investigated catalysts are shown in Fig. 1b. It can be seen that with
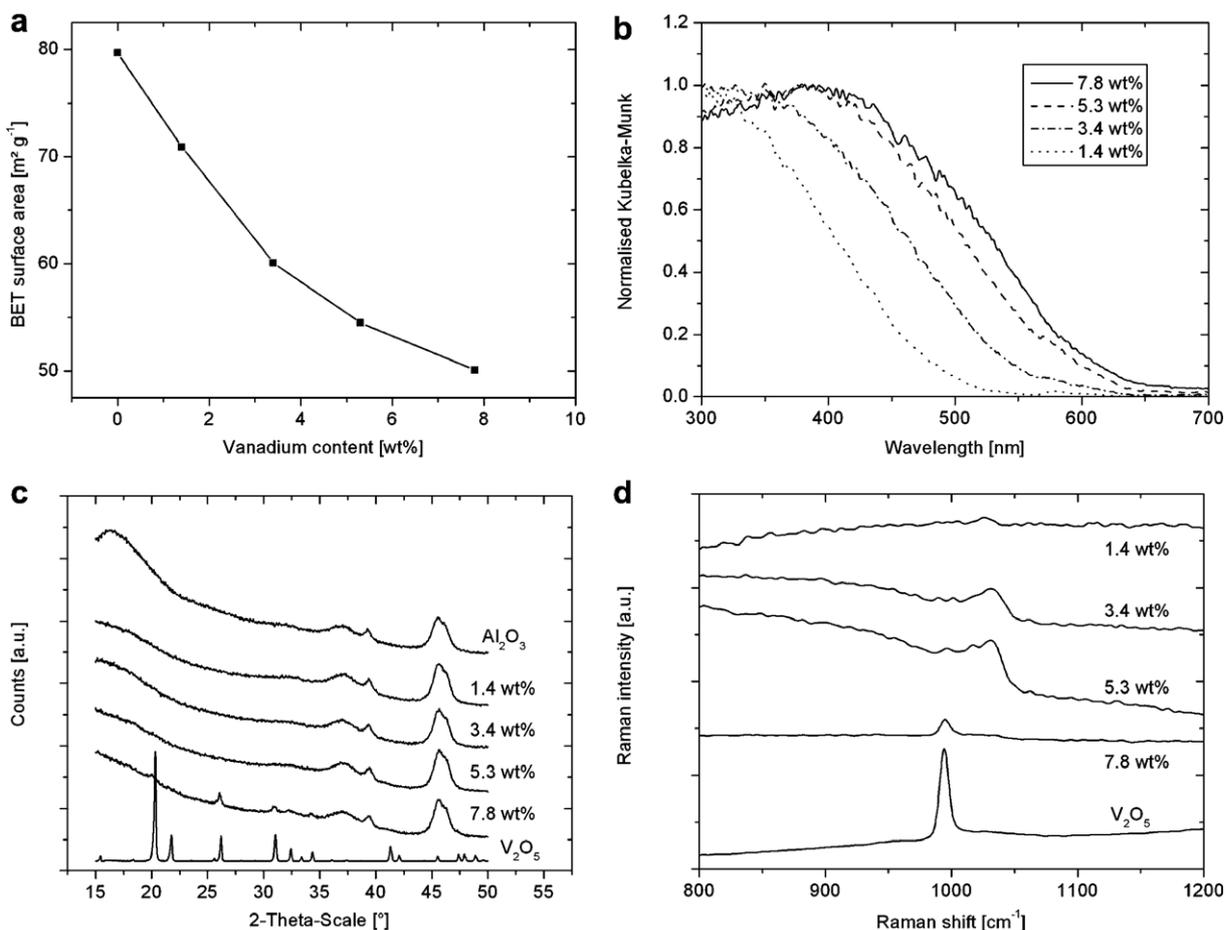
Fig. 1. (a) BET surface area at 77 K, (b) UV/Vis spectra in O_2 flow at 773 K, (c) XRD patterns measured at room temperature, and (d) Raman spectra (recorded at room temperature after dehydration) of investigated VO_x/Al_2O_3 catalyst samples with varying vanadium content; (a) and (c) also contain data of pure γ-Al_2O_3 support material, (c) and (d) also of crystalline V_2O_5.

increasing vanadium content, the characteristic absorbance becomes wider and shifts to higher wavelengths indicating an increasing degree of polymerisation and co-ordination of the VO_x species. By analogy with literature [8,13], it can be concluded that the 1.4 wt% V sample contains well dispersed VO_x species, whereas the 3.4 wt% V sample additionally contains oligomerized, but still dispersed aggregates. The 5.3 and 7.8 wt% V samples are dominated by bands of V–O–V bonds indicating the presence of polymerized and crystalline vanadia bulk phase. However, it is difficult to identify separate vanadia species from this data.

The results of the UV/Vis DRS analysis are confirmed by the XRD patterns of the catalysts that can be seen in Fig. 1c. Independent of the loading, the diffractograms are dominated by broad features of γ-Al_2O_3, which correspond to the diffractogram of the pure γ-Al_2O_3 support shown at the top of the diagram. The diffractogram of crystalline V_2O_5 is given at the bottom of the diagram serving as a reference for crystalline V_2O_5 bulk phase on the catalyst's surface. It has characteristic peaks at $2\theta = 20, 22, 26$, and $31°$. The pattern of crystalline V_2O_5 can be observed only in the 7.8 wt% V sample's diffractogram, but are not detectable for the catalysts with $\leqslant 5.3$ wt% V.

Since sensitivity of X-ray diffraction for crystalline V_2O_5 is limited, the investigated catalysts were further characterized by Raman spectroscopy. The spectral range from 800 to 1200 cm^{-1} is shown in Fig. 1d since characteristic peaks due to the V=O stretching vibration of crystalline V_2O_5 as well as dispersed VO_x species can be detected in this range [13]. At the bottom of Fig. 1d the spectrum of crystalline V_2O_5 is shown as reference. The band at 994 cm^{-1} is a sensitive indicator for crystalline V_2O_5. The catalyst with 7.8 wt% V shows a strong band at 994 cm^{-1} indicating a significant fraction of V_2O_5. However, it should be noted that the Raman cross section of V=O in crystalline V_2O_5 is about 10 times higher than that in dispersed vanadia [13]. Therefore, the shoulder at 994 cm^{-1} in the spectrum of the catalyst with 5.3 wt% V points to the presence of only little crystalline V_2O_5 as compared to the amount of dispersed vanadia (band around 1026 cm^{-1}). The shoulder of the band at 1017 cm^{-1} may indicate a second type of dispersed VO_x species. At a vanadium content of $\leqslant 3.4$ wt% V the band of crystalline V_2O_5 is no more detectable, which strongly suggests that only negligible amounts of crystalline V_2O_5 are present. For the catalyst with 1.4 wt% V, almost no VO_x can be detected due to the low vanadium content.

Catalytic tests were performed in conventional packed bed reactors to obtain thorough information about the catalytic materials before applying them in microstructured reactors.

The catalysts were tested for their activity for propane conversion. This aspect is necessary for the decision towards an appropriate catalyst to be applied in a microstructured reactor.

As can be seen from Fig. 2a, propane conversion increases almost linearly with an increase in modified residence time under isothermal conditions. The catalyst with 7.8 wt% V shows the highest activity followed by the less loaded catalysts. However, the increase of activity with increasing vanadium content does not seem to be linear.

Therefore, the catalysts' activities on the basis of propane conversion per catalyst mass with increasing vanadium content are shown in Fig. 2b. The activity of the investigated VO_x/Al_2O_3 catalysts in the ODP increases with increasing vanadium content. The increase is not linear since in case of the presence of crystalline V_2O_5, a certain amount of vanadia cannot interact catalytically, because it is not accessible for gas phase reactants. The same effect results from clogging of micropores at higher loadings.

Due to limited capacities for loading microstructured reactors with catalytic material, the catalyst with 5.3 wt% V having a rather high activity was chosen for further coating experiments. The use of highly active catalysts is favourable in microreactors, because reaction heat can be dissipated easily due to the high surface to volume ratio of the microstructure.

Additionally to activity aspects, the catalytic materials were tested for selectivity. Selectivity conversion trajectories were measured under isothermal conditions at 723 K only by a variation of residence time. As shown in Fig. 2c, selectivity towards propene is strongly dependent on propane conversion and surface coverage of the support material.

In general, selectivity decreases with increasing conversion because propene is rapidly oxidised to CO and CO_2 [5]. Total oxidation of propane to CO_x can be neglected since the S-axis intercept for all trajectories seems to be nearly 100%, indicating the absence of parallel reactions to the oxidative dehydrogenation. The loss of selectivity goes parallel with increasing surface coverage with vanadia on the support material, in accordance with a study by Argyle et al. [9]. Consequently, the lower selectivity may
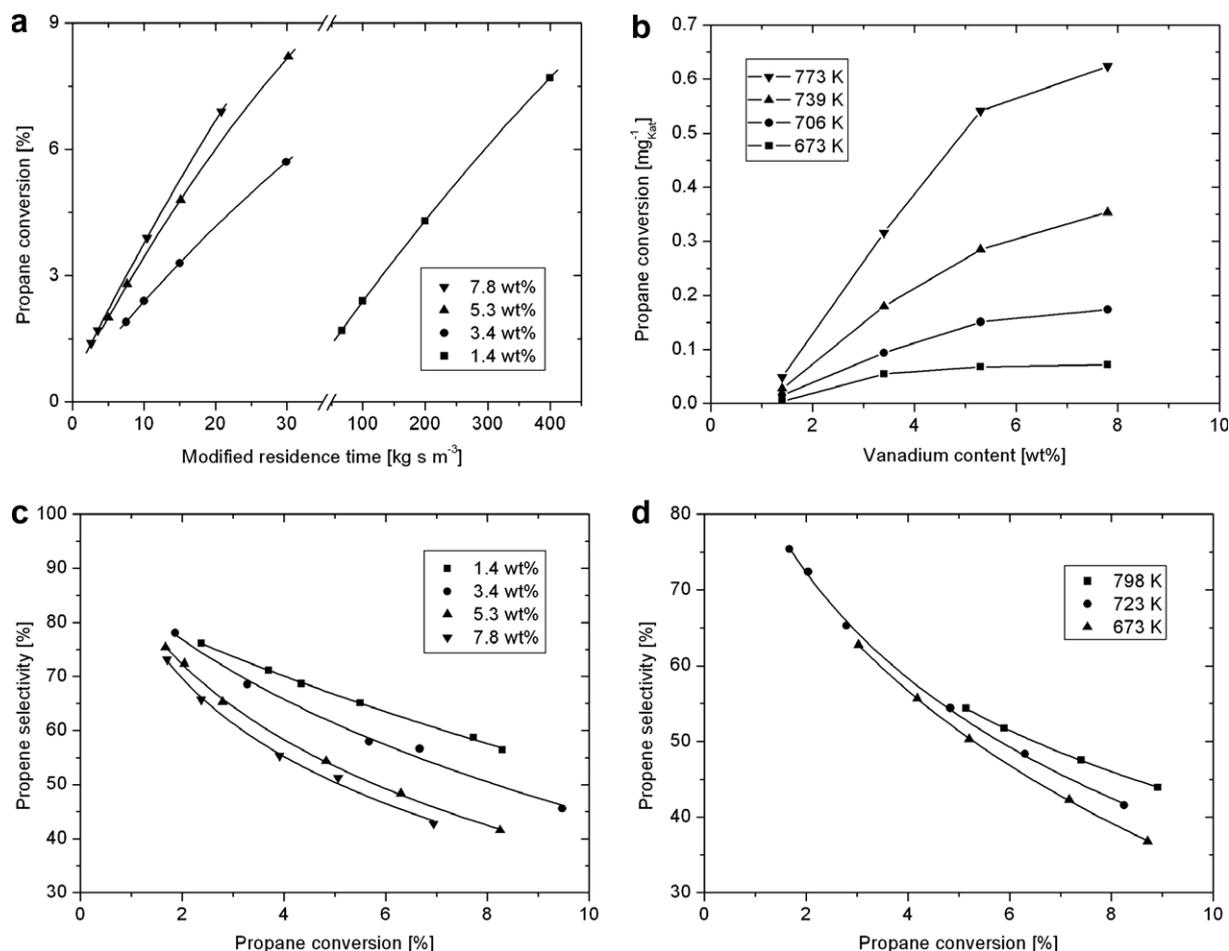
Fig. 2. Catalytic activity for (a) varying modified residence times at 723 K, (b) increasing vanadium content (volume flow 120 ml_n min^{-1}), and selectivity conversion trajectories for (c) differently loaded catalysts at 723 K, and (d) different temperatures for a 5.3 wt% V catalyst, all measured at a constant molar ratio of $C_3H_8:O_2:N_2 = 2:1:4$.

be attributed to the presence of higher polymerized vanadia species and crystalline V_2O_5. It appears that isolated VO_x species and/or smaller aggregates of vanadia provide the highest selectivity in the ODP. This may be explained by the absence of directly neighboured active sites, minimising consecutive combustion of propene at low vanadia loadings. From physico-chemical characterisation, it is difficult to determine the exact structure of the VO_x species. However, with regard to an optimum propene yield, the use of a highly dispersed VO_x/Al_2O_3 catalyst seems to be reasonable, although activity aspects have to be considered (as explained above).

Additionally, the dependence of selectivity on temperature for a 5.3 wt% V catalyst was investigated. As can be seen from Fig. 2d, propene selectivity increases with increasing temperature, which is in good agreement with a previous study of some of the authors [5]. This positive effect seems to be stronger at higher propane conversions. However, the impact of temperature is only weak in comparison to a variation of the vanadium content.

As a first step to transfer the obtained catalysts into microstructured reactors, the catalytic materials were re-suspended in an alcoholic solvent, mixed with additives such as binders (organic and inorganic) and applied as catalytic coatings. The reactors were fabricated by a new method in which, the structured steel platelets are coated with catalyst and soldered at 673 K, giving the reactors sufficient mechanical stability. First catalytic tests were performed in a temperature range from 673 to 873 K. The loading of the reactors (volume = 0.676 cm^3) varied between 10 and 60 mg at volume flows from 30 to 240 ml$_n$ min^{-1}, resulting in modified residence times in the range of 2.5 and 120 kg s m^{-3}. Propane conversions were measured to be 15–20% at total oxygen conversion. The temperature along the catalytic coating was recorded by three thermocouples. The absence of a temperature gradient indicates isothermal reaction conditions. After improving the performance of the catalytic coatings (adhesion, activity, and selectivity), the microstructured reactors will be used to carry out detailed investigations on the ODP with a variation of process parameters in a wider range than would be possible in a conventional packed bed reactor. Initial results show a similar catalytic performance of the coatings under standard conditions in comparison to the original catalyst in fixed bed reactors.

4. Conclusions

VO_x/Al_2O_3 catalytic materials with different vanadia loadings for the application in microstructured reactors have been prepared by a novel preparation method. The materials have been thoroughly characterised to get insight into the degree of vanadia dispersion as a function of vanadia loading. The results from UV/Vis and Raman characterisation indicate that, with increasing vanadium content the formation of polymerized vanadia species is enhanced, whereas starting at a vanadium content of 5.3 wt% V/Al_2O_3 also crystalline V_2O_5 is observed. Catalytic tests in the oxidative dehydrogenation of propane showed higher selectivity with decreasing vanadium content and higher activity with increasing vanadium content. Detailed investigations on the catalytic behaviour of the catalyst applied in microstructured reactors will be subject to future research. The catalyst is also planned to be tested in different microstructures in order to evaluate the influence of the reactor design on catalytic performance.

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