

Reoxidation dynamics of highly dispersed VO_x species supported on γ-alumina

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ABSTRACT

The VO_x/γ-Al₂O₃ catalyst VA-200, which was introduced in a previous article, is further characterized by XPS and visible Raman spectroscopy. The reoxidation of highly dispersed VO_x species with gas phase oxygen is investigated in detail and is described by an empirical kinetic model. It is observed that the reoxidation of reduced VO_x/γ-Al₂O₃ catalyst is strongly affected by the presence of water. The proposed kinetic model includes a distinct coverage of VO_x species with water or hydroxyl groups in the investigated temperature range of 479–712 K. Hydrated surface species are oxidized under release of water. Best fits of the experimental data can be achieved with first order rate laws with respect to oxygen concentration. Experiments are performed in an ideally mixed Berty-type reactor using oxygen step-marking over the reduced catalyst. The evolution of oxygen concentration using the kinetic model is in agreement with the experimentally observed behaviour. The signal of water released during the reaction can be modeled only qualitatively, which (presumably) stems from its sorption behaviour on the acidic alumina support. The oxidation of VO_x species furthermore depends on the reaction temperature. The oxidation of V^{+III} to V^{+V} cannot be completely achieved at temperatures below 673 K. However, the activation energy of this reaction is low, as suggested by the absence of strong variations of the response shapes with respect to temperature.

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1. Introduction

Development and optimization of supported vanadium oxide catalysts have attracted attention because of their activity in several partial oxidation and oxidative dehydrogenation reactions of saturated hydrocarbons [1–3]. These reactions are attractive alternatives towards present processes of olefin production. However, only a few processes have reached industrial application because of the poor selectivity due to consecutive oxidation of the reaction products [4–5].

The catalytic activity of vanadia is attributed to its reducible nature and its ability to easily change its oxidation state from V^{+III} up to V^{+V}. It is strongly influenced by the support material and the vanadia loading [6–8]. The catalytic oxidation obeys the two-step kinetic model developed by Mars and van Krevelen (MvK) [9]. In the first step, the substrate reacts with some lattice oxygen atoms of the supported vanadia catalyst, which is reduced in the process. (The authors are aware of the fact that the MvK mechanism and related terms were developed for V₂O₅ bulk phase catalysts.

However, in conformity with mechanistic aspects and the custom use in literature, the term “lattice oxygen” is used also for vanadyl and bridging oxygen atoms of dispersed non-crystalline VO_x species). The nature of the oxygen atom that is involved in the reaction is still under discussion. Bridging [2,10–12] or vanadyl oxygen atoms [13,14] have been proposed to be the active atom in the oxidation reaction, whereas computational studies have shown that vanadyl oxygen atoms are involved in the rate determining step [15]. In both situations, one or more oxygen atoms are removed from the lattice. Vacancies are then consecutively filled by reaction with gas phase dioxygen molecules in the second step and the catalyst is reoxidized. In the present work it is considered that substrate oxidation and catalyst reoxidation are two independent steps. Many mechanistic studies covered the substrate conversion part whereas only a few studies on the reoxidation process can be found [16–18]. This may partly be due to the ratio of the absolute rates of both parts of the catalytic cycle. Reoxidation is much faster than substrate conversion in general which complicates its investigation by conventional steady state experiments. When reoxidation is not the rate determining step of the overall reaction, the reaction order for oxygen in formal kinetic approaches is low [19–23]. However, the analysis of the reoxidation step is of a fundamental interest.

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Several investigations of the reoxidation of vanadium oxides and vanadia catalysts have been achieved using the temporal analysis of products (TAP) method [16–24], or analysis of transformations of ideal crystal surfaces either spectroscopically [25–28] or theoretically [29,30]. The experimental techniques require idealized ultra-high vacuum and/or clean monocrystal surfaces conditions, which can render the results problematic and contradictory [31]. These differences are well known and denoted with the term “pressure and materials gap”, which has to be negotiated when comparing the results gained from ideal and real systems. With that respect, a recent theoretical study combining DFT and Monte Carlo simulations brought new valuable information concerning the equilibrium structure of alumina supported vanadium oxides [50], but dynamic studies remain challenging.

Water plays an important role in partial oxidation reactions as it is a common product of selective oxidation reactions. Also, water vapor is often added to the feed to improve the catalyst performance. Previously it has been shown for vanadium containing catalysts that the presence of steam can significantly reduce the barrier for propane activation and/or shift the product spectrum from propylene to acrylic acid [32–34]. From a fundamental point of view, this raises questions about the value of the sticking coefficient of water on the catalyst surface at elevated temperatures.

In several studies on the microkinetics of the oxidative dehydrogenation of propane (ODP) at ambient conditions, the rates within the Mars–van Krevelen mechanism are modeled with 0.5th and 1st orders for oxygen and reduced vanadia sites, respectively [20,35,36]. Because reoxidation is fast compared to substrate conversion, these reaction orders were not determined experimentally but were based on schematic mechanistic considerations. However, 1st rate order for oxygen partial pressure gives also reasonable fitting results [11,37,38].

Stated models for reoxidation predict simple reaction schemes including one or two elementary steps. However, these models were assumed for ambient experimental conditions, or gained from investigations under idealized conditions (TAP). Up to now, no experimental approach confirms these assumptions under “non-ideal” conditions. The Berty-type reactor is a powerful tool for the investigation of the reoxidation step under ambient conditions. Isothermic conditions and ideally mixed gas phase combined with tracer step experiments allow new insights into this elementary reaction step in vanadia catalyzed oxidation reactions.

Among several differently supported VO_x catalysts prepared under comparable conditions the alumina supported sample showed the best catalytic performance in ODP with respect to propene selectivity [39]. The $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst VA-200, introduced in a recent article [19], was thereby chosen for this study, however, a similar investigation is projected for low loaded SiO_2 (SBA-15) supported vanadium oxide samples [40].

2. Experimental

2.1. Catalyst preparation and characterization

Low loaded $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst grains were prepared by wet saturation–impregnation of a commercial porous γ -alumina support with vanadyl acetylacetonate in toluenic solution. The method is described in a recent publication containing also fundamental characterization and catalytic performance in the oxidative dehydrogenation of propane (ODP) [19]. The characterization techniques, namely N_2 -physisorption, X-ray diffraction (XRD), inductively coupled plasma spectroscopy (ICP-OES), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), temperature programmed reduction (TPR), and O_2 -titration, are described there. The resulting physico-chemical characteristics gained from

Table 1

Physico-chemical data of the low loaded $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst.

Property	Method	Result
BET surface area	N_2 -physisorption	$106.6 \text{ m}^2 \text{ g}^{-1}$
Average pore diameter	N_2 -physisorption	15.7 nm
Phase composition	XRD	$\gamma\text{-Al}_2\text{O}_3$
Chemical composition	ICP-OES	1.4 wt.% V
Surface composition (atomic ratio)	XPS	O: 61.2%, V: 2.5%, C: 3.8%, Al: 32.5%
Vanadia surface concentration	O_2 -titration	$1.55 \text{ V atoms nm}^{-2}$
State of vanadia species	TPR, UV–vis DRS, Raman spectroscopy	Highly dispersed

the application of these methods and from additional characterization by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) are assembled in Table 1.

In our previous study [19], oxygen titration of all vanadia species quantified by ICP was conducted at 773 K to test and confirm their accessibility for reaction with gas phase reactants. The present study implies a characterization of the redox-behaviour by varying the reoxidation temperature between 479 and 713 K. Further characterization of the vanadia species and their distribution is performed using XPS and Raman spectroscopy (see Supplementary material).

2.2. Catalytic experiments in a Berty-type reactor

Catalytic experiments were performed in a Berty “Micro” reactor purchased from Autoclave Engineers[®]. This internal cycle reactor is designed with a fixed, circular, and screened catalyst bed and a top mounted vane type blower. Gas circulation is directed downward along the vessel wall and deflected upward through the catalyst bed. The basket volume and the free vessel volume are 3.6 and 15.4 cm^3 , respectively. The model used in this study is made of inert HASTELLOY[®] C-276 and designed for temperatures up to 800 K at a pressure of 345 bar. Ideal mixing conditions inside the vessel were proven by tracer step experiments switching the feed between N_2 and O_2 . For this purpose the catalyst basket was filled with inert alumina grains with particle sizes similar to that of the catalyst (100–300 μm). The resulting concentration profiles for ambient conditions were detected by on-line mass spectrometry (MS) as shown in Fig. 1. A rotation speed of at least 4000 min^{-1} is required for ideal gas phase mixing for flow rates up to 100 $\text{mL}_n \text{ min}^{-1}$, below this value a weak bypass flow can be observed. The ideally mixed reactor volume determined this way is in the range of $13 \pm 0.5 \text{ mL}$, which is in good agreement with the data given by the supplier.

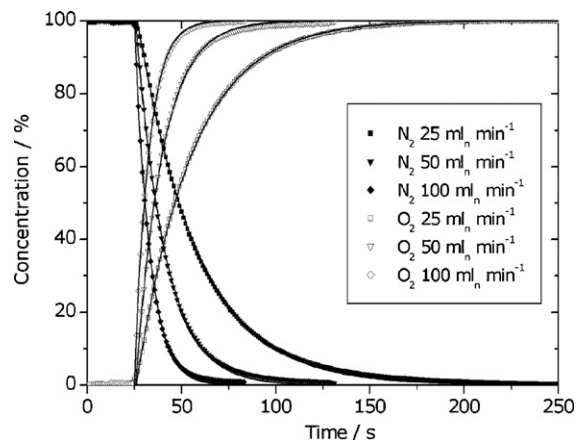


Fig. 1. Residence-time distribution of the Berty reactor from tracer step experiments switching the feed from nitrogen to oxygen at different flow rates; fit of the data with exponential decay functions (full lines).

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