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Structure of flame-made vanadia/silica and catalytic behavior in the oxidative dehydrogenation of propane

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ABSTRACT

Vanadia/silica particles with a specific surface area up to 330 $m^2\,g^{-1}$ and a V_2O_5 content up to 50 wt.% or V surface density up to 27.6 V nm^{-2} were prepared by flame spray pyrolysis. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature-programmed reduction, Raman spectroscopy, and ^{51}V MAS NMR and tested in the oxidative dehydrogenation (ODH) of propane. Depending on vanadia content, different vanadia species were formed. The as-prepared flame-made catalysts showed dominantly isolated monomeric VO_x surface species for V loadings exceeding even the typical “monolayer coverage” (2 V nm^{-2}) of classic wet-impregnated materials. The stability of these VO_x species depended on temperature and V surface density. Catalysts with 3.3 V nm^{-2} were stable up to 500 °C and those with 2 V nm^{-2} up to 600 °C. Catalysts loaded with 3–25 wt.% V_2O_5 were tested for the ODH of propane. Catalysts containing $\geqslant$15 wt.% V_2O_5 showed structural rearrangement of the VO_x species during the catalytic tests inducing a transition from monomeric to crystalline vanadia. The turnover frequency of flame-made catalysts decreased with increasing vanadia loading, indicating a higher activity of monomeric VO_x species compared to crystalline V_2O_5. The conversion (global activity), however, showed a maximum for the 20 wt.% V_2O_5/SiO_2 (4.6 V nm^{-2}) catalyst. The selectivity to propene depended mainly on propane conversion and only to a lesser extent on the structure of the VO_x species. Highest selectivity (55%) was achieved for the low loaded catalysts. With increasing vanadia loading, formation of CO_x increased and the product ratio of CO_2/CO decreased. Highest propene yield was measured for catalysts with relative high V surface density containing both monomeric VO_x and crystalline V_2O_5. Flame spray pyrolysis proved to be a very versatile method for synthesis of V_2O_5/SiO_2 catalysts with high dispersion of isolated VO_x species at high surface density.

1. Introduction

Propene is one of the most important feedstock in the chemical industry as it is used for the synthesis of various chemical intermediates and major processes such as polypropene (PP) synthesis. Polypropene is used for the production of diverse products, ranging from solvents to plastics. At the present time, steam cracking, fluid-catalytic-cracking, and catalytic dehydrogenations are the main processes to gain olefins from natural feedstock oil [1]. Increasing oil prices and growing PP market (4–5% per year) spur the development of a less energy-intensive process for the propene production [2]. One of the promising processes is the oxidative dehydrogenation (ODH) of propane to propene. This process will allow to use propane of natural gas stocks, in a range of 2–5% [3], as a feedstock for the propene/PP production.

Catalyst based on supported vanadia showed promising results for the ODH reaction. It is commonly agreed that vanadium oxide can be present on the support oxide in three distinct forms: i.e. as monomeric VO_x species at low loadings (typical <2.3 V nm^{-2}), as oligomeric form at medium loadings (2.3–7.5 V nm^{-2}), and as V_2O_5 crystals at high loadings (>8 V nm^{-2}) [4–7]. The composition of VO_x species and thus the catalytic behavior of supported vanadia catalysts are influenced by the specific surface area (SSA), V_2O_5 content, the composition of the support [6,8–10], and also by the synthesis method [11–13]. For SiO_2-supported catalysts, the transition from amorphous monomeric to crystalline vanadia occurs already at low V surface densities around 2 V nm^{-2} [10] or even lower [2,14], without exhibiting any oligomeric VO_x species in the transition range.

The activity of vanadia species in the ODH reaction can depend significantly on the supporting oxide [6,10]. The role of the structure of the VO_x species on the support surface on activity and selectivity is still debated and not completely resolved. Khodakov et al. [6] stated that oligomeric VO_x species or even small V_2O_5 crystallites are more active and selective than isolated monomeric sites independent of the supporting oxide (TiO_2, SiO_2, Al_2O_3, ZrO_2, and HfO_2). Tian et al. [10] stated that the relative rate of propene

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formation does not depend on the nature of the support (SiO_2, Al_2O_3, and ZrO_2), or V surface density and structure (mono- and oligomeric), in agreement with previous studies [15]. For silica-supported vanadia-based catalysts, however, several authors reported turn-over-frequencies that differ up to one order of magnitude depending on V surface density. Monomeric VO_x species were identified as the most active and selective V sites in the ODH of propane [2,14,16–18].

Most of these catalysts were prepared using classic, multiple-step, wet-phase processes (e.g. impregnation) of the corresponding non- or mesoporous support. Good accessibility of the VO_x species is important for high activity and selectivity. The dispersion and structure of the VO_x species and thus their catalytic performance depend not only on the composition of the supporting oxide but also on the catalyst synthesis method, like vapor-fed flame synthesis [19], flame spray pyrolysis [11,13], sputter deposition [20], or atomic layer deposition [12]. Especially the wet-chemistry synthesis routes sometimes show broad variation in the structure of the VO_x species depending on the synthesis conditions.

A highly reproducible synthesis method leading to easy accessible model catalysts of high purity is flame spray pyrolysis (FSP), a one-step process suitable for producing mixed metal-oxide catalysts with excellent control of particle morphology and reproducibility [13,21–23]. In the FSP process, the VO_x is formed on the oxide support surface due to the lower melting point (~700 °C) of V_2O_5 compared to the oxide supports (melting point usually >1000 °C). The vanadia layer is formed when the flame temperature is low enough for it to condense out in vapor-fed [13,19] and liquid-fed flame synthesis [13]. With this process, catalysts with significant differences in particle structure and VO_x species composition can be produced. FSP-made V_2O_5/TiO_2 catalysts exhibit monomeric and oligomeric VO_x species at high V surface densities where the corresponding wet-made catalysts form crystalline VO_x species [13]. Recently, V_2O_5/SiO_2 catalysts were prepared by flame pyrolysis [11] that showed a relative low surface area ($<80\ m^2\ g^{-1}$) for flame-made silica-supported materials [24,25] and a high V dispersion in the bulk of the particles which can probably be traced to their use of low enthalpy solvents and low dispersion of the liquid precursor that may have resulted in catalysts by droplet-to-particle formation rather than nucleation from the gas phase [23]. Only 30% of the nominal V atoms were accessible for the reaction. Particularly, the low vanadia content catalysts showed almost no selectivity to propene [11]. The aim of the present work was to explore the potential of flame spray pyrolysis for synthesis of non-porous, nanostructured V_2O_5/SiO_2 catalysts for the oxidative dehydrogenation of propane (ODH). A focal point was the effect of FSP synthesis on the structural properties of V_2O_5/SiO_2 catalysts and catalytic performance. For this purpose, catalysts with different V loadings were prepared, characterized with various physicochemical techniques, and tested in ODH.

2. Experimental

2.1. Catalyst preparation

Nanostructured vanadia/silica particles were made by FSP of appropriate precursor solutions [13,26]. For the vanadium precursor, ammonium metavanadate (Sigma–Aldrich, 99%) was mixed with 2-ethylhexanoic acid (2-EHA, Riedel-de Haën, >99%) and acetic anhydride (Riedel-de Haën, >99%) in a ratio of 2:1 under stirring and heating it to 100 °C for several hours resulting in a metal concentration of 0.5 M. Then, appropriate amounts of hexamethyldisiloxane (Aldrich, >98%) and the vanadium precursor were mixed based on the nominal weight content vanadia in the catalyst (0–50 wt.%) with xylene (Riedel-de Haën, >96%) and 2-EHA (Riedel-de Haën, >99%) in a ratio of 1:1 resulting in a total metal concentration of $0.75\ mol\ L^{-1}$. The use of solvents (xylene, 2-EHA) with significantly higher combustion enthalpy ($\approx 4600\ kJ\ mol^{-1}$) ensured high enthalpy density in the flame and particle formation via nucleation from the gas phase [27,28]. Moreover, the O_2 pressure drop was adjusted to 1.7 bar for high dispersion of the liquid precursor spray and the flow rates (enthalpy) of the pilot flame were tripled (CH_4: $1.5\ L\ min^{-1}$, O_2: $3.3\ L\ min^{-1}$) compared to Rossetti et al. [11]. Solubility and stability of the metal precursors were no problem for the whole investigated range of vanadia contents.

This precursor solution was fed by a syringe pump (Inotec, IER-560) through the FSP nozzle and dispersed by O_2 (PanGas, 99.95%, $5\ L\ min^{-1}$) into a fine spray that was ignited and sustained by a premixed CH_4/O_2 flame. Additional $5\ L\ min^{-1}$ of sheath O_2 was fed in the reactor to ensure complete combustion. A detailed description of the laboratory scale FSP reactor can be found elsewhere [26]. The powders were collected with the aid of a vacuum pump (Busch SV 1050 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diamater).

2.2. Catalyst characterization

The specific surface area (SSA, $m^2\ g^{-1}$) of the powder was determined by nitrogen adsorption (Pan Gas, >99.999%) at 77 K using the Brunauer–Emmett–Teller (BET) method (Micromeritics Tristar 3000) with a five point-isotherm ($0.05 < p/p_0 < 0.25$). Accounting for the V_2O_5 content in the powder density, the average particle size (d_{BET}) was calculated assuming spherical particles. Full BET adsorption–desorption isotherms were measured on the same instrument. X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min^{-1}, Cu Kα radiation).

Temperature-programmed reduction (TPR) was used for determination of the average oxidation state (AOS) after reduction and reducibility of vanadia. Experiments were carried out on a Micromeritics Autochem II 2920 equipped with a TCD-detector by flowing 5 vol.% H_2 in Ar (Pan Gas, >99.999%, $10\ mL\ min^{-1}$) through the sample. The temperature was increased from 50 to 950 °C at $10\ °C\ min^{-1}$. Prior to this analysis, the sample was oxidized in flowing oxygen (PanGas, >99.999%, $20\ mL\ min^{-1}$) at 500 °C for 30 min to assure complete oxidation of vanadium species.

Raman spectroscopy was performed (Renishaw InVia Reflex Raman) with a 514-nm diode (Ar-ion laser, 25 mW) laser as excitation source focused with a microscope (Leica, magnification 50×). For the dehydrated Raman analysis, an *in-situ* cell equipped with a quartz window was used [13]. The samples were pressed into tablets and placed in the cell and then directly heated up to 500 °C under flowing synthetic air (PanGas, 99.999%, $40\ mL\ min^{-1}$). The spectra were recorded at 500 °C for 40 s and 20 accumulations to obtain sufficient signal-to-noise ratio and collected on a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 12.5-mW laser energy.

The ^{51}V MAS NMR experiments were performed at room temperature on a Bruker MSL-400 spectrometer at a resonance frequency of 105.25 MHz using a 4-mm MAS NMR probe. NMR measurements were taken on as-prepared (hydrated) and on dehydrated samples. In the latter case, the catalysts were treated in a furnace at 500 °C ($10\ K\ min^{-1}$) for 2 h under vacuum, subsequently transferred without any contact to air into a glove box purged with dry N_2 and filled into the 4-mm MAS rotor. In the experiments, a single pulse length of $\pi/8$ and a relaxation delay of 0.5 s, and a spinning rate of ca. 12.5 kHz were used. The ^{51}V chemical shift was referenced to vanadium trichloride oxide ($VOCl_3$). The NMR data were processed with the Bruker software WINNMR. Anisotropic shift values were obtained from the simulated MAS NMR spectra with the Bruker WINFIT software.