Ceramic foams directly-coated with flame-made $V_2O_5/TiO_2$ for synthesis of phthalic anhydride


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ABSTRACT

Flame-made airborne $V_2O_5/TiO_2$ nanoparticles were deposited directly onto mullite foam supports making ready-to-use catalysts for the o-xylene conversion to phthalic anhydride. These particles containing 10 % w/w $V_2O_5$ were made by combustion of liquid precursor sprays and characterized by transmission electron microscopy, nitrogen adsorption, X-ray diffraction (XRD), temperature programmed reduction (TPR) and Raman spectroscopy.

$V_2O_5/TiO_2$ nanoparticles were produced in single step by flame spray pyrolysis having a sub-monolayer, monomeric and polymeric $V_2O_5$ on the titania surface. The specific surface area, the titania and vanadia composition were thermally stable up to 450°C.

Catalyst structure was controlled in situ during deposition through the pressure drop across the foam resulting in homogeneous to patchy $V_2O_5/TiO_2$ coatings. The produced foam catalysts needed no subsequent treatment like calcination as for common wet-made catalysts and could be installed in the reactor for the catalytic evaluation. The coated-foam catalyst revealed higher catalytic activity and similar selectivity to phthalic anhydride at high o-xylene conversion compared to a wet-made catalyst. Directly coated foam catalysts combine high accessibility, high catalytic yield with favorable support structures (low pressure drop, enhanced heat transfer) and fast production routes, making them attractive for catalytic reactions.

Keywords: flame-spray pyrolysis, direct deposition, ceramic foam, partial oxidation, vanadia/titania

1 INTRODUCTION

The partial oxidation of o-xylene on $V_2O_5/TiO_2$ catalysts with $O_2$ from air in multiple parallel fixed bed reactors is a highly exothermic reaction (1300 to 1800 kJ mol$^{-1}$ o-xylene) with a world-wide phthalic anhydride (PA) production of over 3.7 million tons per year (1996) [1]. The PA is an important intermediate product in manufacture of commodity chemicals such as modifiers for rubber and polymers. During its synthesis, evolving heat has to be transferred effectively out of the catalyst bed because hot spots above 500 °C deactivate the catalyst irreversibly [2] and lead to an increased risk of thermal reactor runaway. Usually for this reaction, "egg-shell" vanadia/titania catalysts of millimeter size with solid, inert cores are packed into a fixed bed. The thickness of the catalytically active shell amounts up to 100 μm typically [3]. This catalyst type is used to prevent activity and PA selectivity reduction by mass transfer limitations inside the porous catalyst. However, high pressure drop over low porosity (40 to 45 %) packed beds containing these catalyst pellets often limits the PA productivity [4]. The pellet shape affects the catalyst bed porosity, so hollow cylinders or rings are used commonly to keep the pressure drop as low as possible [5]. An alternative is the application of ceramic foams as catalyst supports [6]. Such foams offer the possibility to improve reactor performance especially for highly exothermic and fast chemical reactions as heat transfer is enhanced compared to packed beds of spherical or cylindrical pellets [7]. The open-pore structure and the high void fraction, up to 95 %, of ceramic foams lead to a lower pressure drop and an increased heat transfer by radiation compared to packed beds [6]. In contrast to the laminar, separated flow in honeycombs, radial gas dispersion and higher gas turbulence is possible increasing heat and mass transfer in the structure [6, 8]. In addition, thermal conductivity and surface properties of the support can be selected from a large variety of foam materials [9] so that foams can combine properties of packed beds and honeycombs [6, 7]. Besides support structures the $V_2O_5/TiO_2$ catalyst itself has a big influence on the catalytic performance. A high dispersion of vanadia on titania, enabling a good accessibility of vanadia, is crucial for high activity. Monomeric and polymeric vanadia species showed enhanced reactivity in selective oxidations compared to crystalline vanadia [10]. However, the vanadia species that will result in highest activity and selectivity has not been identified yet [11] and might also depend on the reaction conditions [12]. Vanadia/titania catalysts have been made already in vapor-fed flames (4 – 200 g h$^{-1}$) resulting in high anatase fractions (>90 wt. %), containing 0 – 10 wt.% $V_2O_5$ of high dispersion [13] and specific surface areas ranged from 23 – 120 m$^2$ g$^{-1}$ [14]. Flame-made catalysts exhibited an open-pore structure that might facilitate mass transfer limited reactions compared to wet-made catalysts [15]. Flame-
spray pyrolysis (FSP) in particular, is a versatile process for producing mixed-metal oxides of nanoscale size and a promising technique for catalyst production [15]. Very recently it has been shown that direct deposition of flame-made materials can lead to highly efficient sensors [16]. Extending this to catalysis by combining the two steps of particle production by FSP and direct particle deposition on catalytic support (e.g. foams) may shorten the catalyst synthesis chain thereby reducing production costs. The direct deposition of airborne nanoparticles on ceramic foam supports may lead to a different pore size structure [17] and porosity [16] than obtained by standard multi-step wet coating techniques. The open-pore structure may be retained, promoting the gas penetration into the active layer. Such flame-deposited layers exhibit good adhesion and thermal contact to the support [18] and porosities around 98% [16].

Here ready-to-use catalysts were produced by direct deposition of FSP-made V_2O_5/TiO_2 nanoparticles on ceramic (mullite) foam supports.

2 EXPERIMENTAL

Xylene (Fluka, >98.5%) and acetonitrile (Fluka, >99.5%) solvents were mixed (11:5 by volume) with appropriate amounts of titanium tetraisopropoxide (TTIP, Aldrich >97%) and vanadium oxo-triisopropoxide (Strem Chemicals, >98%), resulting in titanium metal concentrations ranging from 0.1 to 3.4 (without solvent) mol L⁻¹ and a V_2O_5 content of 10 wt.% in the powder product [19].

Vanadia/titania mixed oxides were synthesized by FSP in a laboratory-scale reactor [20] being a concentric two-phase nozzle with a capillary (inner diameter of 0.42 mm) through which the liquid precursor was fed by a syringe pump (Inotec, IER-560). Through the 1st annulus (inner/outter diameter 0.71/0.95 mm) 5 L min⁻¹ of dispersion gas (O₂, Pan Gas, 99.95%) was fed with a pressure drop of 1.5 bar. The resulting spray was ignited by a circular premixed flame (inner diameter 10 mm, slit width 10 μm) of CH₄ (1.5 L min⁻¹, Pan Gas 99.95%) and O₂ (3.2 L min⁻¹). An additional O₂ sheath flow (5 L min⁻¹) for complete combustion of the precursor was supplied through a ring of sinter metal (inner/outter diameter 11/18 mm). All gas-flow rates were adjusted by calibrated mass-flow controllers (Bronkhorst). Powders were collected on glass microfibre filters (Whatman GF/D, 257 mm in diameter) by a vacuum pump (Busch SV 1025 B). The production rates ranging from 0.1 to 3.4 (without solvent) mol L⁻¹ and a V_2O_5 content of 10 wt.% in the powder product [19].

For comparison a 10 wt.% vanadia/titania reference catalyst was prepared also by standard impregnation [21]. Flame-made vanadia/titania was pelletized at 70 MPa, crushed and sieved, having the same agglomerate size range as for the wet-made V_2O_5/TiO_2. In the following these compacted catalysts and the wet-made ones are referred to as pellet catalysts.

The partial oxidation of o-xylene was performed in an isothermal, laboratory scale fixed bed reactor with plug flow behavior at 367°C. The reactor consisted of a vertically installed stainless steel tube of 16 mm inner diameter and a length of 380 mm that was electrically heated. Pressure in the reactor was adjusted to 1.3 bar. The molar fraction of o-xylene and oxygen in the reactor feed were 0.005 and 0.2, respectively. Total gas-flows ranged from 120 to 600 mL min⁻¹ at standard conditions. Modified residence times (τ_{mod}, g_{cat} s cm⁻³) were defined as mass vanadia/titania in the reactor divided by the total gas-flow under reaction conditions (367°C, 1.3 bar).
3 RESULTS

The SSA of the powders decreased from 195 ($d_{\text{BET}} = 8 \text{~nm}$) to 53 m$^2$ g$^{-1}$ ($d_{\text{BET}} = 29 \text{~nm}$) with increasing $V_2O_5/TiO_2$ production rate (not shown) from 2.6 g h$^{-1}$ up to 89.6 g h$^{-1}$ respectively, as observed for vapor-fed flame-made $V_2O_5/TiO_2$ [14] and liquid-fed flame-made materials, in general. Increasing particle-precursor concentration in the flame favors particle coagulation and coalescence, reducing the overall specific surface area [22]. The calcined wet-made reference sample had 8 m$^2$ g$^{-1}$ SSA ($d_{\text{BET}} = 200 \text{~nm}$) being smaller than all FSP-made powders. Particles with 93 m$^2$ g$^{-1}$ were used for FSP-made pellets, retaining their SSA after pressing during pellet preparation [23].

The TEM (Figure 1a) shows flame-made $V_2O_5/TiO_2$ (17.2 g h$^{-1}$) corroborating the open pore structure of the material. No micrometer size particles were found by TEM analysis indicating a homogeneous particle size distribution. The electron diffraction pattern (Figure 1a inset) confirms the crystalline structure of these particles.

Figure 2 compares TPR signal intensities from as-prepared FSP-made and calcined wet-made $V_2O_5/TiO_2$. The FSP-made powders showed one distinct reduction peak with a maximum intensity ($T_{\text{max}}$) at 483°C as observed for vapor-fed flame made $V_2O_5/TiO_2$ [13]. Broadening of peaks indicated anatase nanosized crystals of 17 to 29 nm. The anatase size increased with increasing production rate from 10 nm up to 29 nm having the lowest anatase content of 82 wt.% at production rate of 2.6 g h$^{-1}$ and anatase contents $>94$ wt.% for production rates above 17.6 g h$^{-1}$ $V_2O_5/TiO_2$. The calcined, wet-made catalyst showed in contrary peaks of 4 wt.% crystalline vanadia with a crystal size of 56 nm.

First vanadia crystal structures for FSP-made vanadia/titania are observed at sinter temperatures $>500^\circ$C. The phase transformation of anatase crystals into rutile crystals above 500°C can also be observed: the peak intensity corresponding to anatase decreased while the peak intensity corresponding to rutile increased. After sintering at 600°C only rutile was detected which corresponded to Raman results (not shown).

FSP-made vanadia/titania nanoparticles were in-situ deposited onto mullite foams Figure 1b) resulting in homogeneous to patchy coatings (Figure 1c). Coated foams with high SSA $V_2O_5/TiO_2$ showed the highest activity of all catalysts. Pellets of FSP-made catalysts reached full conversion after 0.004 to 0.02 g s cm$^{-3}$, faster by at least one order of magnitude than wet-made pellets (0.18 g s cm$^{-3}$). Vanadia/titania with low SSA (53 m$^2$ g$^{-1}$, not shown) resulted in less active catalyst than powder with high SSA. No significant differences in catalytic activity were found for catalysts with homogeneous and patchy (not shown) coatings of low SSA vanadia/titania. FSP-made pellets of high SSA particles showed lower activity compared to the coated foams with high SSA vanadia/titania [23].

4 DISCUSSION

Vanadia/titania nanoparticles with high anatase content (94%) were made at high production rates ranging from 17.9 to 89.6 g h$^{-1}$ by flame spray pyrolysis. Having a significantly higher SSA, flame-made $V_2O_5/TiO_2$ provides more external surface area than the wet-made material. This resulted in monomeric vanadia species on the surface of the flame-made particles. Peak TPR temperatures below 500°C indicate monomeric vanadia on titania, being reduced more easily than polymeric ($T_{\text{max}} \approx 540^\circ$C) or bulk ($T_{\text{max}} > 580^\circ$C) vanadia [10]. Sintering flame-made $V_2O_5/TiO_2$ for 5h (5°C min$^{-1}$) did not change titanate composition or crystallinity up to 450°C. Starting at 500°C the anatase started transforming into rutile and at 600°C that phase change was completed [25]. The vanadia phase com-
position on TiO₂ did not change significantly for sinter temperatures up to 450°C. The first vanadia crystal structures were detected above 500°C. At higher sinter temperatures, the vanadia phase composition changed from the dominantly amorphous mono- and polymeric to crystalline bulk vanadia (650°C).

The FSP-made pellet catalyst showed slightly lower activity than the coated foams with high SSA. Smaller pore sizes and longer diffusion times through the pellets may have led to inner mass transfer limitations decreasing selectivity at high conversions and activity compared to coated foams [23].

5 CONCLUSIONS

Titania containing 10 wt.% vanadia nanoparticles were produced in single step by flame spray pyrolysis having a sub-monolayer, monomeric V₂O₅ on the titania surface. The specific surface area and vanadia composition were thermally stable up to 450°C. For higher sinter temperatures the SSA decreased drastically by TiO₂ phase transformation and grain growth.

Direct deposition of flame-made vanadia/titania on mullite foams was controlled by the pressure drop over foam/filter, resulting in patchy to nearly homogeneous coatings of V₂O₅/TiO₂ on the foam. The coated-foam catalyst revealed higher catalytic activity and similar selectivity to phthalic anhydride at high o-xylene conversion compared to a wet-made catalyst. The high vanadia distribution and its monomeric composition on the open foam structure facilitated vanadia accessibility. Homogeneous/patchy coatings of V₂O₅/TiO₂ with low specific surface area showed slightly higher yield than the homogeneous coatings with high specific surface area but with lower space-time-yield. Directly coated foam catalysts combine high accessibility, high catalytic yield with favorable support structures (low pressure drop, enhanced heat transfer) and fast production routes, making them attractive for catalytic reactions [23].

REFERENCES