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Publication date:
2011

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Citation (APA):

Høj, M., Jensen, A. D., & Grunwaldt, J-D. (2011). Flame made V/Al₂O₃ propane oxidative dehydrogenation catalyst. Abstract from 10th EuropaCat Congress , Glasgow, United Kingdom.

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Flame made V/Al₂O₃ propane oxidative dehydrogenation catalyst

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Introduction

Liquid fed flame spray pyrolysis (FSP) is a novel one-step synthesis method for nano-sized particles, which is particularly interesting for mixed oxides [1]. For this organo-metallic compounds dissolved in an organic solvent are sprayed with high velocity oxygen and ignited with a small premixed methane-oxygen flame [2]. The solvent and metal precursors evaporate and combust to form atomically dispersed vapours, which nucleate to form clusters when reaching cooler parts of the flame. The formed clusters grow by surface growth and coalescence, accompanied by sintering [3]. This results in nanoparticles which coagulate and sinter to form agglomerates and aggregates with high inter particle porosity [1].

Demands for short chain olefins like ethene and propene are expected to increase in the near future [4]. Current production methods include steam cracking, fluid catalytic cracking and catalytic dehydrogenation. Oxidative dehydrogenation of propane to propene is another option. This exothermic reaction could be operated autothermally, however, a catalyst with sufficient activity and selectivity for industrial production of propene has not been discovered yet [4]. Promising catalyst candidates are supported vanadium and molybdenum oxide, where supports like Al₂O₃, SiO₂, TiO₂, ZrO₂, MgO and ZrO₂ or mixtures thereof have been used [4]. In this study a FSP made VO_x/Al₂O₃ catalyst has been synthesized and tested.

Experimental

Alumina supported vanadia was prepared by FSP by spraying a solution of vanadium oxy-tris(*iso*-propoxide), aluminium tris(*sec*-butoxide) and acetylacetonate dissolved in xylene, $c_{\text{metal}} = 0.35$ M, at 5 ml/min with 5 Nl/min oxygen dispersion gas. Specific surface area was measured by 6 point BET ($p/p_0 = 0.05 - 0.25$), XRD using Ni filtered Cu K α radiation and TEM was recorded on a Technai T20 microscope. Catalytic activity was measured in a tubular flow reactor with 4 mm i.d. using 50 mg of catalyst diluted with 340 mg SiC to a bed length of 20 mm. Gas flow was 100 to 250 Nml/min with C₃H₈/O₂/N₂ = 10/10/80. The furnace temperature was 480 °C resulting in a bed temperature of 497 °C. Outlet gas composition was analysed using a GC with TCD and FID detectors for permanent gasses and hydrocarbons, respectively.

Results/Discussion

The FSP prepared V/Al₂O₃ catalyst consisted of γ -Al₂O₃ with XRD amorphous vanadia phase. It contained 9 wt.% V₂O₅ (5 wt.% V) with alumina balance. The specific surface area of

catalyst was 189 m²/g, which is equivalent to an average particle size of 8.1 nm assuming spherical particles. TEM images showed the particles as hexagonally truncated spheres (Fig. 1). Analysis of 124 particles showed a particle size of 9.5 ± 2.4 nm after fitting to a log-normal distribution, which is in reasonable agreement with the BET particle size. The apparent vanadia surface density was 3.1 VO_x/nm². Catalytic activity measurement of the catalyst at 497 °C is shown in Table 1 and Fig. 1. Moderate conversion of propane was observed with reasonably good selectivity to propene. Since the space velocity is high and the initial concentration is intermediate this results in excellent productivity of propene [4]. The selectivity to propene increases while the conversion and selectivities to CO and CO₂ decrease with increasing space velocity. The selectivities sum to less than 100 %, especially at high space velocity, probably due to formation of oxygenated species not detected with the current GC setup.

Table 1: Catalytic activity and selectivity of the flame made VO_x/Al₂O₃ catalyst. ^a

GHSV ^b (Nl kg _{cat} ⁻¹ h ⁻¹)	Conversion (%)		C-based selectivity (%)				STY ^c (kg _{C₃H₆} kg _{cat} ⁻¹ h ⁻¹)
	C ₃ H ₈	O ₂	C ₃ H ₆	C ₂ H ₄	CO	CO ₂	
120·10 ³	19.4	49.5	40.4	0.3	38.3	16.5	1.87
180·10 ³	14.5	28.5	43.1	0.2	28.2	12.4	2.23
240·10 ³	11.2	18.6	45.7	0.2	23.3	10.2	2.44
300·10 ³	9.4	14.1	46.9	0.2	20.2	9.1	2.62

^a Conditions: T = 497 °C, $m_{\text{cat}} = 50$ mg, F = 100-250 Nml/min, C₃H₈/O₂/N₂ = 10/10/80. ^b Gas hourly space velocity. ^c Space time yield (productivity of propene per hour per kg catalyst).

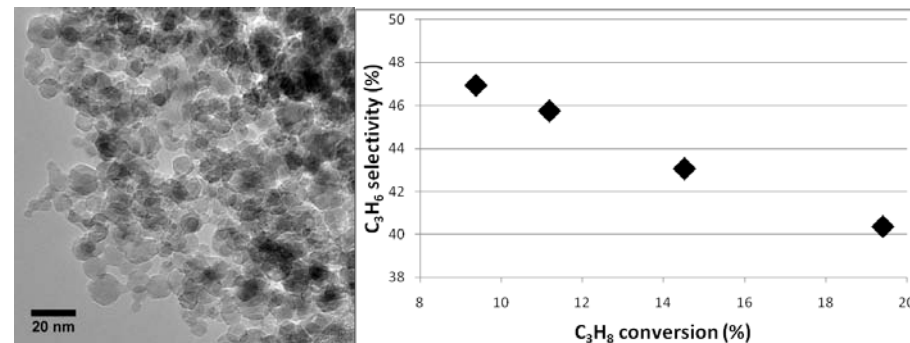


Figure 1: TEM image of the as prepared flame made VO_x/Al₂O₃ catalyst. Propene selectivity as function of propane conversion.

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