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

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Motivation

Vanadia-based catalysts are promising catalyst for the application in oxidative dehydrogenation of propane [1]. Besides the composition of the support, the structure of the VO_x-species is crucial for the catalytic performance. Tetrahedral monomeric species are considered to be most favorable for high catalytic activity [2]. Recently, flame-made vanadia-based catalysts showed high V dispersion even at high vanadium surface density [3]. Here we studied the V_2O_5/SiO_2 system made by flame spray pyrolysis (FSP) for the oxidative dehydrogenation of propane.

Catalyst Morphology

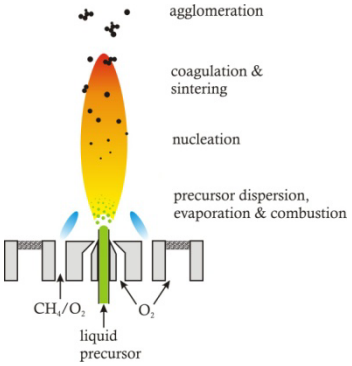

Fig. 1 Flame spray pyrolysis (FSP) synthesis set-up and working principle.

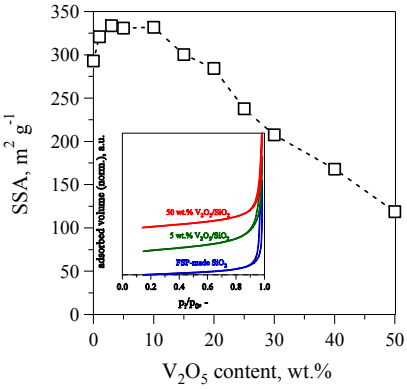

Fig. 2 Influence of vanadia content on specific surface area (SSA) of the single step FSP-made catalyst. Inset shows BET isotherms indicating non-porous particles [4].

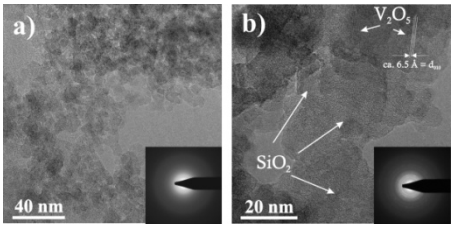

Fig. 3 TEM images of the 10 wt.% (a) and 50 wt.% (b) V_2O_5/SiO_2 samples. Only amorphous particles are detected for the 10V-Si catalysts while the 50V-Si sample clearly shows the presence of crystalline domains (EDX inset) which can be attributed to crystalline V2O5 with lattice fringes of ca. 6.5 Å [4].

Structure of VO_x specie

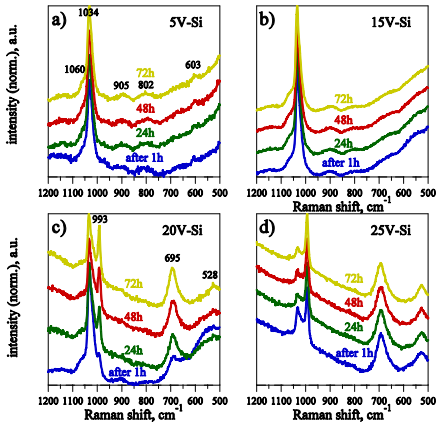

Fig. 4 Long term *in-situ* Raman spectra recorded at 500 °C in synthetic air for 72h for the 5V-Si (a), 15V-Si (b), 20V-Si (c) and 25V-Si (d) catalysts [4].

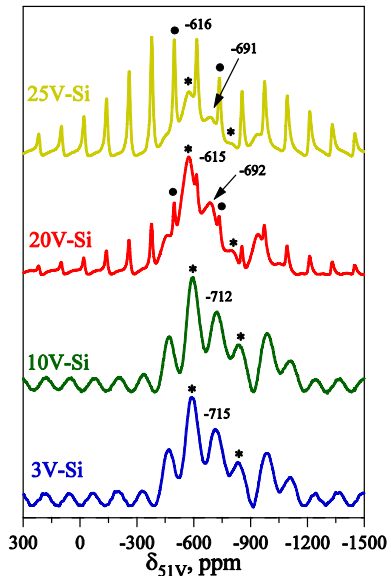

*Fig. 5 ^{51}V MAS NMR spectra of the 3V-, 10V-, 20V- and 25V-Si catalysts under dehydrated conditions. Symbols ● and * indicate the sidebands of the isotropic shifts at -616 ppm (V-O-V) and -690 or -711 ppm (V-O-Si), respectively [4].*

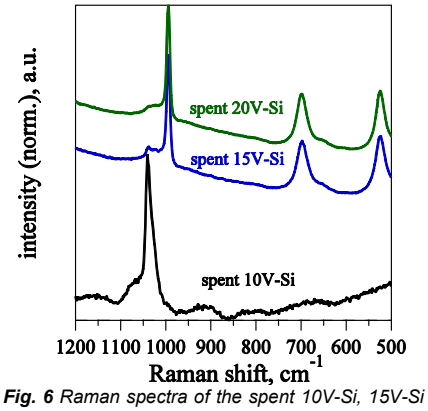

Fig. 6 Raman spectra of the spent 10V-Si, 15V-Si and 20V-Si catalysts dehydrated at 500 °C [4].

Catalysis

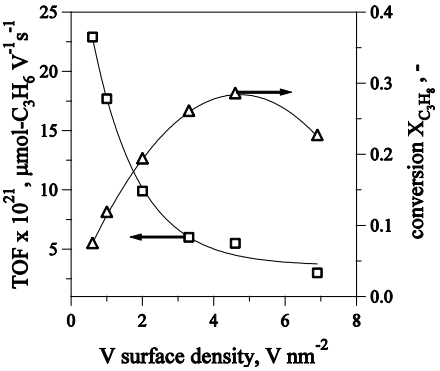

Fig. 7 Variation of the turnover frequencies (TOF, cubes) and propane conversion (X_{C3H8}, triangles) with the V surface densities. Reaction conditions: m_{cat} = 0.2 g, GHSV = 45'000 L $g_{cat}^{-1}h^{-1}$, $T_{reaction}$ = 550 °C, $C_3H_8:O_2:N_2$ = 1:1:3 [4].

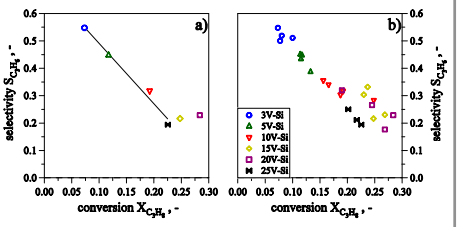

Fig. 8 Propene selectivity as function of propane conversion on flame-made V_2O_5/SiO_2 catalysts for (a) constant GHSV (45'000 L $g_{cat}^{-1}h^{-1}$) and (b) with variation of GHSV (37'500-60'000 L $g_{cat}^{-1}h^{-1}$) [4].

Sample	C_3H_8 conv. (%)	Selectivity (%)			TOF x 10^{21} (µmol-C_3H_6 $V^{-1}s^{-1}$)	STY_{C3H6}[b] (kg $kg_{cat}^{-1}h^{-1}$)
		C_3H_6	CO_2	CO		
0V-Si	3.7	40.4	36.0	5.9	-	0.3
3V-Si	8.5	50.0	34.6	9.2	29.3	0.9
5V-Si	11.5	43.4	29.0	12.2	22.5	1.1
10V-Si	16.6	34.0	25.6	23.5	12.2	1.2
15V-Si	23.7	33.2	26.4	22.3	11.7	1.8
20V-Si	19	31.2	21.9	25.4	6.9	1.4
25V-Si	20.2	25.0	24.1	32.1	4.6	1.1

Tab. 1 Conversion and selectivity of the flame-made V_2O_5/SiO_2 catalysts in the oxidative dehydrogenation of propane at 550 °C [4].

Conclusions

- FSP-made catalysts show unique properties in terms of V dispersion with dominantly isolated tetrahedral sites up to 3.3 V nm^{-2}
- VO_x species are highly stable up to 500°C
- Activity strongly depended on the amount of vanadia and increased with reaction temperature and loading
- Highest propene yield was achieved despite presence of crystalline V_2O_5

References

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