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Supporting Information for:

A Molecular Precursor Route to Active and Selective Vanadia-Silica-Zirconia Heterogeneous Catalysts for the Oxidative Dehydrogenation of Propane

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Synthesis of $OV[OSi(O^tBu)_3]_3$. At room temperature, 1.156 g of $OVCl_3$ (0.067 mol) was added rapidly to a vigorously stirred solution of 1.7 mL of pyridine and 5.28 g of $HOSi(O^tBu)_3$ in 75 mL of benzene. Stirring was continued for 24 h, after which the pyridinium hydrochloride was removed by filtration and washed with 50 mL of hexanes. After removal of the volatile material from the combined extracts, 5.25 g of $OV[OSi(O^tBu)_3]_3$ (92%) was obtained as a pure, white crystalline powder. The compound thus isolated may contain small amounts of $HOSi(O^tBu)_3$ as an impurity. Further purification by recrystallization from 20 mL of CH_2Cl_2 at -40 °C resulted in isolation of 4.85 g of analytically pure $OV[OSi(O^tBu)_3]_3$ (85% yield). Anal. Calcd for $C_{36}H_{81}O_{13}SiV$: C, 50.44; H, 9.52. Found C, 50.58; H, 9.59. ^1H NMR (300 MHz, C_6D_6): δ 1.51 (s). ^{13}C NMR (75.5 MHz, C_6D_6): δ 31.89, 73.35. ^{29}Si NMR (99.35 MHz, C_6D_6) δ -98. ^{51}V NMR (131.54 MHz, C_6D_6) δ -777. UV-vis (hexanes) 253 nm, ε 9800. IR (Nujol, CsI) 2960 s, 2920 s, 2850 s, 1460 s, 1388 s, 1364 vs, 1242 s, 1212 w, 1190 vs, 1070 vs br, 1028 m sh, 1008 m sh, 910 vs br, 832 m, 806 w, 702 s, 670 w, 490 m, 470 m, 421 w, 378 w, 308 vw br. MS (EI, 40eV) 935 (0.5), 857 (0.3), 841 (0.2), 727 (2), 671 (7), 615 (15), 559 (35), 503 (54), 447 (86), 391 (100), 335 (50).

Synthesis of V/Si/Zr/O xerogels. A pyrex tube was charged with $OV[OSi(O^tBu)_3]_3$, $Zr(OCMe_2Et)_4$, and octane (ca. 10 mL for each 1.5 g of precursor mixture) in the ratios given in Table

1, and the tube was then flame-sealed under vacuum. The resulting solution was heated at 175 °C for 48 h to yield a gel (except for the homothermolysis of $OV[OSi(O^tBu)_3]_3$, which was heated at 180 °C for 120 h). The xerogels were obtained by air-drying for 3-7 days. Before catalysis, the materials were calcined under a gentle flow of oxygen at 500 °C for 3 h.

Catalysis. Selectivity and conversion measurements were carried out in a fixed-bed quartz reactor using 0.025-0.100 g of catalyst mixed with 0.500 g of quartz chips. The reactions were carried out at under ambient pressure with a feed ratio $O_2/C_3H_8/He$ of 8:25:200. C_3H_8 conversion was varied by changing the flow rate between 30 and 233 mL h^{-1}. On-line analysis of reactants and products was performed using a Hewlett-Packard 5880 gas chromatograph equipped with a carboxen column. Only C_3H_6, H_2O, CO and CO_2 were detected as reaction products. Exact catalyst amounts used: 25, 32, 25, 32, 45, 85, 100 mg for V/Si/Zr/O catalysts containing 33, 23, 18, 14, 10, 5 and 2 % V_2O_5 respectively, 60 mg for the catalyst form ref. 27, and 25 mg for the reference V/Si/Zr/O catalyst made by wet impregnation with $NH_4(VO_3)$ and oxalic acid.

Table 2. Comparison of the best catalytic systems for propane ODH. Data from different references should be compared with caution, since they were typically obtained under different reaction conditions (flow rates, reactor design, etc.).

	Activity [mmol·g^{-1}h^{-1}]	**Activity** [mmol·m^{-2}h^{-1}]	**Selectivity** [% C_3H_6]	**Conversion** [% C_3H_8]	**T** [°C]	Reference
Mg/V/O	1.82	0.22	62	20	500	6,9
Nb/V/O	0.89	0.3	70	10	394	10
V-silicalite	1	0.0022	51	22	500	6,12
β–$NiMoO_4$	5.6	0.75	78	7	500	11
$MgMoO_4$	0.50	0.172	61	16	500	7
$CoMoO_4$	0.63	0.068	89 (61)	5 (20)	450	7
V_2O_5/ZrO_2 10% V_2O_5	58	0.48	43	10	500	28
V/Si/Zr/O 14% V_2O_5	100	0.21	77	6	500	this work
V/Si/Zr/O 18% V_2O_5	78	0.27	87	4	500	this work

Figure 3. Diffuse Reflectance UV-vis spectra for V/Si/Zr/O catalysts with different vanadia contents.

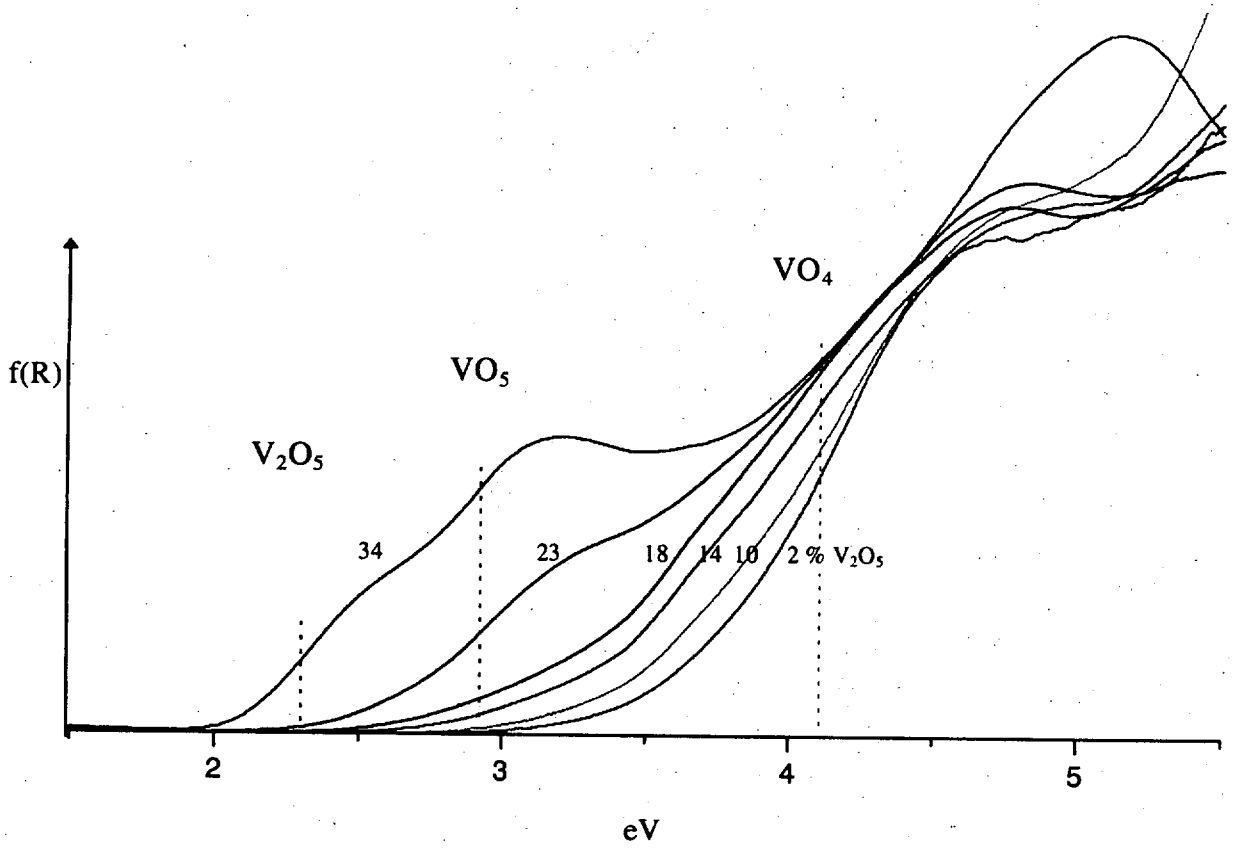


Figure 4 FT-IR of V/Si/Zr/O catalysts

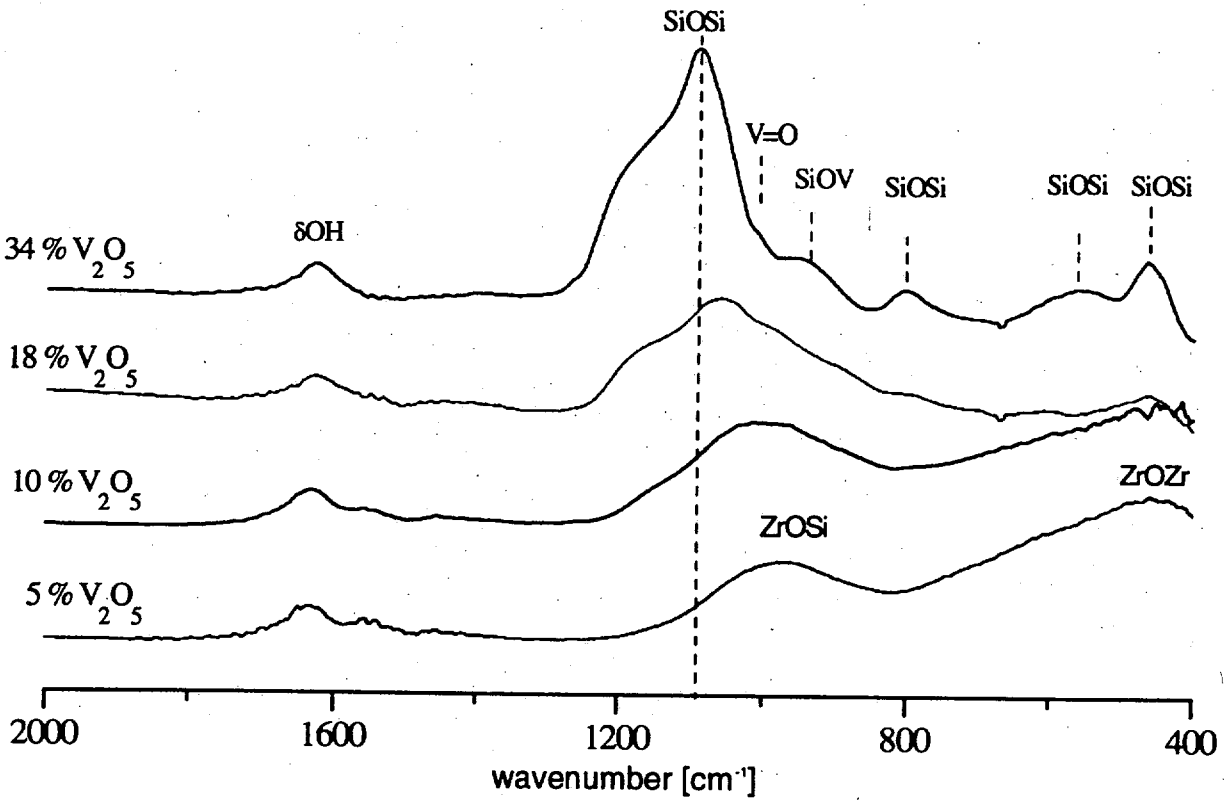
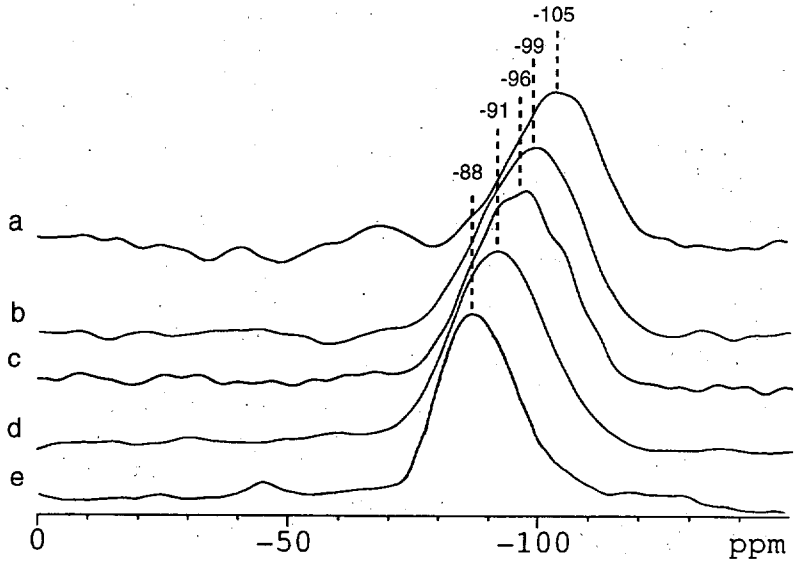


Figure 5. Solid-State MAS ^{29}Si NMR spectra of V/Si/Zr/O xerogels.



a 46% SiO_2, 23% V_2O_5, 31% ZrO_2, δ = -104 ppm

b 36% SiO_2, 18% V_2O_5, 46% ZrO_2, δ = -99 ppm

c 28% SiO_2, 14% V_2O_5, 58% ZrO_2, δ = -96 ppm

d 20% SiO_2, 10% V_2O_5, 70% ZrO_2, δ = -91 ppm

e 10% SiO_2, 5% V_2O_5, 85% ZrO_2, δ = -104 ppm