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

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A major challenge in chemistry is the design and development of new catalysts for selective transformations of saturated hydrocarbons.[1−3] For example, the high demand for C2−C4 alkenes has motivated interest in their production from inexpensive C1−C4 alkanes. The direct, dehydrogenation of light alkanes proceeds only at high temperatures, where cracking and coking present serious problems. On the other hand, oxidative dehydrogenation (ODH) is thermodynamically favored at lower temperatures and does not suffer from the deposition of carbon, which decreases catalyst performance.[1] Thus, the ODH of propane (eq 1) is attractive as an alternative source of propene, particularly given its high demand for the production of polypropene, acrylonitrile, and propene oxide.[4] However, this selective oxidation is particularly challenging, given the high reactivity of propene toward further oxidation.[1,5] Among the best catalysts reported for the ODH of propane[1,3,6] are $CoMoO_4$,[7] $MgMoO_4$,[7] Mg/V/O,[8,9] V/Nb/O,[10] $NiMoO_4$,[11] and vanadia silicalite.[6,12]

$$\mathrm{CH_3CH_2CH_3} + {}^1/{}_2\mathrm{O_2} \xrightarrow[\text{catalyst}]{} \mathrm{H_2C{=}CHCH_3} + \mathrm{H_2O} \quad (1)$$

In search of synthetic methods that allow atomic-level control over the local environment of reaction centers in mixed-metal catalysts, we are investigating molecular precursor routes to heterogeneous catalysts for the ODH of propane. Along these lines, we have previously reported the conversion of metal−OSi(O^{t}Bu)$_3$ derivatives to high surface area, highly dispersed metal oxide−silica materials.[13−15] The approach described here focuses on vanadia as the active component, since vanadia silicalite has been reported as one of the most selective catalysts for propane ODH.[6] More specifically, we describe the solution-phase transformation of a two-component precursor system, $OV[OSi(O^tBu)_3]_3$ (**1**) and $Zr(OCMe_2Et)_4$ (**2**), to vanadia−zirconia−silica catalysts that exhibit impressive activities and selectivities for the ODH of propane. The presence of zirconia−silica in these catalysts was expected to improve the vanadia dispersion[16] while providing high surface areas.[13,14]

Precursor **1** was obtained in 92% yield by reaction of $OVCl_3$ with $HOSi(O^tBu)_3$ in the presence of pyridine.[17] Cothermolysis of various ratios of **1** and **2** in octane solution at 175 °C produced gels that were dried in air and then calcined under O_2 for 3 h at 500 °C, to quantitatively produce highly porous, amorphous V/Si/Zr/O xerogels containing 2−34% vanadia (eq 2). The porosities and surface areas of these xerogels vary with elemental composition (Table 1). Whereas the average pore size and total pore volume increased with increasing vanadia content, the highest surface areas were obtained for a sample composed of ca. 10% vanadia, 20% silica, and 70% zirconia.[18] In general, this method provides materials with properties approaching those observed for aerogels.[19] Infrared spectra of the V/Si/Zr/O xerogels, in the region containing asymmetric Si−O−Si and Zr−O−Si stretches (700−1250 cm^{-1}), resemble those reported for zirconia−silica aerogels shown to be highly dispersed.[20] For materials with a high vanadia content (≥18%), a band at ca. 950 cm^{-1} is observed for the V−O−Si stretch[21,22] and bands at 450, 550, and 800 cm^{-1} can be assigned to silica.[23] The position of the O→V charge-transfer band edge, measured by DRUV (Diffuse Reflectance UV−vis) spectroscopy, was correlated with the vanadium coordination environment.[24,25] For xerogels with 2−8% vanadia, an absorption edge of ca. 4.1 eV is consistent with single-site, 4-coordinate vanadium. Xerogels with 10−18% vanadia exhibit a gradual shift in the absorption edge from ca. 4.0 to ca. 3.6 eV, indicating an increasing degree of linear polymerization for the VO_4 tetrahedra.[25] For the sample containing 23% vanadia, band-edge features at ca. 3.6 and 2.9 eV suggest the additional presence of 5-coordinate vanadium, and only for the vanadia−silica xerogel (34% vanadia) was a prominent feature observed for crystalline V_2O_5, at ca. 2.3 eV. The samples with <23% vanadia exhibit MAS ^{29}Si NMR shifts (δ −99 to −88) that reflect primarily contributions from Q^2 and Q^3 sites, and therefore a high degree of silicon dispersion.[26]

$$\underset{\mathbf{1}}{n\mathrm{OV[OSi(O^tBu)_3]_3}} + \underset{\mathbf{2}}{m\mathrm{Zr(OCMe_2Et)_4}} \xrightarrow[-\mathrm{C_4H_8},\ -\mathrm{C_5H_{10}},\ -\mathrm{H_2O}]{\text{octane/175 °C/48 h}} \mathrm{V}_n\mathrm{Si}_{3n}\mathrm{Zr}_m\mathrm{O}_x\mathrm{(OH)}_y \quad (2)$$

The results of the propane ODH catalysis are summarized in Figure 1 and Table 1. The vanadia−silica xerogel exhibits low activity and rapidly declining selectivity, as found for V_2O_5,[27] but the introduction of zirconia dramatically improves the catalyst performance. In contrast to what has been observed for vanadia−silica catalysts,[27] the selectivity to propene increases for the V/Si/Zr/O catalysts with increasing V_2O_5 content. The best performance was observed for xerogels with 18% and 23% vanadia, which are characterized by high selectivities comparable to the

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(1) Kung, H. H. *Adv. Catal.* **1994**, *40*, 1.

(2) Warren, B. K.; Oyama, S. T. *Heterogeneous Hydrocarbon Oxidation*; American Chemical Society: Washington, DC, 1996; Vol. 638.

(3) Albonetti, S.; Cavani, F.; Trifiró, F. *Key Aspects of Catalyst Design for the Selective Oxidation of Parafins*; Marcel Dekker: New York, 1996.

(4) Thayer, A. M. *Chem. Eng. News* **1997**, *March 24*, 20.

(5) Bettahar, M. M.; Costentin, G.; Savary, L.; Lavalley, J. C. *Appl. Catal. A* **1996**, *145*, 1.

(6) Cavani, F.; Trifiro, F. *Catal. Today* **1995**, *24*, 307.

(7) Yoon, Y. S.; Ueda, W.; Moro-oka, Y. *Top. Catal.* **1996**, *3*, 265.

(8) Chaar, M. A.; Patel, D.; Kung, H. H. *J. Catal.* **1988**, *109*, 463.

(9) Gao, X.; Ruiz, P.; Guo, X.; Delmon, B. *J. Catal.* **1994**, *148*, 56.

(10) Smits, R. H. H.; Seshan, K.; Leemreize, H.; Ross, J. R. H. *Catal. Today* **1993**, *16*, 513.

(11) Mazzochia, C.; Aboumrad, C.; Diage, C.; Tempesti, E.; Herrmann, J. M.; Thomas, G. *Catal. Lett.* **1991**, *10*, 181.

(12) Centi, G.; Trifiro, F. *Appl. Catal. A* **1996**, *143*, 3.

(13) Terry, K. W.; Tilley, T. D. *Chem. Mater.* **1991**, *3*, 1001.

(14) Terry, K. W.; Lugmair, C. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 9745.

(15) Lugmair, C. G. Ph.D. Thesis, U.C. Berkeley, 1997.

(16) Sohn, J. R.; Cho, S. G.; Pae, Y. I.; Hayashi, S. *J. Catal.* **1996**, *159*, 170.

(17) Terry, K. Ph.D. Thesis, UC San Diego, 1993.

(18) The relative weight percentages of the metal oxides in the xerogels were calculated from the precursor mixtures which undergo thermolysis quantitatively.

(19) Schneider, M.; Baiker, A. *Catal. Rev.* **1995**, *37(4)*, 515.

(20) Miller, J. B.; Ko, E. I. *J. Catal.* **1996**, *159*, 58.

(21) Luca, V.; MacLachlan, D. J.; Morgan, K. *Chem. Mater.* **1997**, *9*, 2720.

(22) Twu, J.; Shih, C.-F.; Guo, T.-H.; Chen, K.-H. *J. Mater. Chem.* **1997**, *7*, 2273.

(23) Kornatowski, J.; Wichterlova, B.; Jirkovski, J.; Loefller, E.; Pilz, W. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1067.

(24) Morey, M.; Davidson, A.; Eckert, H.; Stucky, G. *Chem. Mater.* **1996**, *8*, 486.

(25) Schrami-Marth, M.; Wokaun, A.; Pohl, M.; Krauss, H.-L. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2635.

(26) (a) Wies, C.; Meise-Gresch, K.; Müller-Warmuth, W.; Beier, W.; Göktas, A. A.; Frischat, G. H. *Phys. Chem. Glasses* **1990**, *31*, 138. (b) Luca, V.; MacLachlan, D. J.; Morgan, K. *Chem. Mater.* **1997**, *9*, 2720.

(27) Mamedov, E. A.; Corberán, C. *Appl. Catal. A* **1995**, *127*, 1.

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Table 1. Characterization Data and Catalytic Activities for V/Si/Zr/O Xerogels and Two Reference Catalysts

n:m[a]	$V_2O_5/SiO_2/ZrO_2$ wt (%)[b]	BET surface area[c] (m^2/g)	total pore vol (cm^3/g)[c]	av pore size (Å)[c]	activity[d] ($mmol\ g^{-1}\ h^{-1}$)	
					673 K	773 K
0.032	2/4/93	430 (302)	0.50	23.1	3.1	17
0.064	5/10/85	553 (428)	0.57	20.6	9.1	45
0.14	8/15/77	647 (436)	0.68	21.0	14	70
0.19	10/20/70	638 (447)	1.1	28	15	88
0.32	14/28/58	529 (466)	1.4	56	28	100
0.51	18/36/46	414 (404)	1.61	82	15	78
1.03	23/46/31	239 (268)	0.97	81	7.6	46
∞	34/66/0	320 (311)	2.25	140	2.2	19
10% V_2O_5 on ZrO_2[28]	10/0/90	260 (122)			18	58
18% V_2O_5 on ZrO_2/SiO_2[e]	18/36/46	(121)	(0.29)	(51)	0.3	0.9

[a] Molar ratio of precursor **1** and **2** in the thermolysis mixture. [b] For $V_nSi_{3n}Zr_mO_{(8.5n+2m)}$ as the formed composition after calcination. [c] The number in parantheses is the surface area after calcination at 500 °C. [d] Fixed bed microreactor, 0.020−0.100 g of catalyst + 0.500 g of quartz sand, $O_2/C_3H_8/He$ = 8/25/200 mL min^{-1}. [e] Prepared by NH_4VO_3−oxalic acid wet impregnation of a Si/Zr/O xerogel (see text).

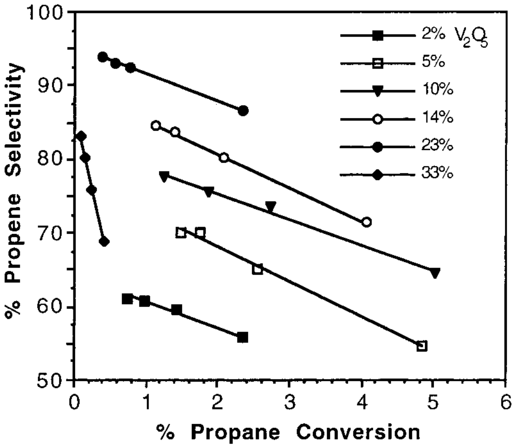

Figure 1. Plot of selectivity to propene as a function of propane conversion, with V/Si/Zr/O xerogel catalysts (at 673 K).

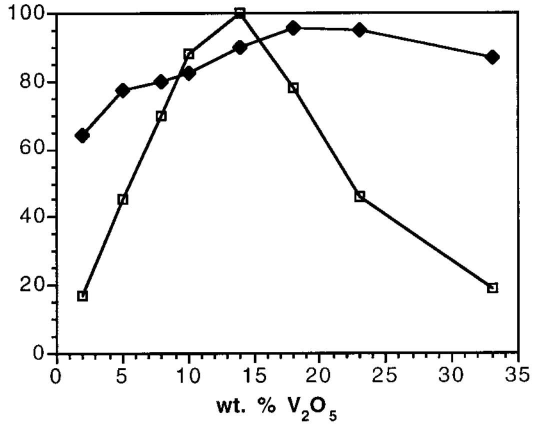

Figure 2. Correlation of vanadia content with activity (□, mmol h^{-1} g^{-1} at 773 K) and propene selectivity (◆, % at 673 K, extrapolated to 0% conversion) for the V/Si/Zr/O catalysts.

best yet reported for propane ODH.[1,3,6−12] Interestingly, the selectivities observed for these catalysts at 0% conversion are invariant over the temperature range of 400−500 °C. For the catalyst with 18% V_2O_5, 8.0% conversion of propane (with 20% conversion of O_2) at a propene selectivity of 81.5% was achieved at 550 °C. The zirconia-containing xerogels exhibit selectivities for propene that decrease rather slowly with conversion, indicating that the presence of zirconia suppresses the competing, deleterious oxidation of propene in these structures. Activities for the V/Si/Zr/O catalysts are presented in Table 1 and Figure 2. The highest activity was observed for the catalyst containing 14% vanadia. Figure 2 correlates selectivities and activities for the catalysts, and shows that high activities are achieved for the most selective catalyst (18% vanadia). On a per-gram basis, the activities of these catalysts far exceed those previously reported for propane ODH catalysts (by factors of ≥18), however, β-$NiMoO_4$[11] is approximately three times as active on the basis of catalyst surface areas. Significantly, the activity and selectivity exhibited by the catalyst with 18% V_2O_5 were constant at 500 °C over a 2 h period, and during this time the catalyst surface area was reduced by only 15%.

To evaluate the utility of this molecular-precursor route to catalysts, we compared data obtained from materials with a similar composition, but prepared by more conventional methods (impregnation). A high surface area, active V_2O_5/ZrO_2 catalyst prepared by NH_4VO_3−oxalic acid wet impregnation of ZrO_2 was found to exhibit optimal performance at a loading of 10% V_2O_5,[28] and exhibited a selectivity at 400 °C that is comparable to the V/Si/Zr/O catalyst containing 5% V_2O_5. In addition, at low conversion, the V_2O_5/ZrO_2 catalyst exhibited a decreasing selectivity with increasing temperature. A second catalyst for comparison, with 18% vanadia, was prepared by NH_4VO_3−oxalic acid wet impregnation of a zirconia−silica xerogel, which was obtained via cothermolysis of $Zr[OSi(O^tBu)_3]_4$[14] and $Zr(OCMe_2Et)_4$. This catalyst exhibited a very low activity (Table 1), and a selectivity of ca. 80% at low conversions. Thus the molecular precursor, cothermolysis procedure of eq 2 produces a catalyst with superior and unique properties.

In summary, a novel method for the preparation of high surface area, ternary metal oxide catalysts, has been developed. The V/Si/Zr/O catalysts with 18 and 23% V_2O_5 compare favorably to the most selective and active catalysts reported for propane ODH,[1,3,6−12] and exhibit catalytic properties which are superior to those of previously reported vanadium-based catalysts. This method is inherently versatile, allows control over elemental composition, and should be applicable to many catalyst formulations. Most significantly, the novel features and impressive performance for these materials suggest that molecular-level control over structure can provide new generations of superior catalysts.

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Supporting Information Available: Synthetic procedures and characterization data and IR, solid state ^{29}Si NMR, and DRUV spectra for the V/Si/Zr/O catalysts (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(28) Khodakov, A.; Yang, J.; Su, S.; Iglesia, E.; Bell, A. T. *J. Catal. A* **1998**, *177*, 343.