In Situ UV–Vis–NIR Diffuse Reflectance and Raman Spectroscopy and Catalytic Activity Studies of Propane Oxidative Dehydrogenation over Supported CrO\textsubscript{3}/ZrO\textsubscript{2} Catalysts

T. V. Malleswara Rao and Goutam Deo*

Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208 016, India

Jih-Mirn Jehng

Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, Republic of China

Israel E. Wachs

Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

Received February 17, 2004. In Final Form: May 3, 2004

The molecular structures, oxidation states, and reactivity of 3 and 6% CrO\textsubscript{3}/ZrO\textsubscript{2} catalysts prepared by incipient wetness impregnation were examined under different conditions. The in situ Raman spectroscopic studies under dehydrated conditions reveal that the 3 and 6% CrO\textsubscript{3}/ZrO\textsubscript{2} catalysts possess equal amounts of monochromate and polychromate species. Consequently, monolayer coverage on this ZrO\textsubscript{2} support is about 3% CrO\textsubscript{3}. The 6% CrO\textsubscript{3}/ZrO\textsubscript{2} possesses an additional Raman band due to Cr\textsubscript{2}O\textsubscript{3} crystals corresponding to the remaining 3% CrO\textsubscript{3}. Furthermore, during reaction conditions the polychromate species is preferentially reduced, the monochromate species are slightly affected, and the Cr\textsubscript{2}O\textsubscript{3} crystals are not affected. The in situ UV–vis–NIR diffuse reflectance spectroscopy results reveal that under steady-state reaction conditions the extent of reduction and edge energy position of surface Cr\textsuperscript{6+} cations increase with an increase in reduction environment for the 3 and 6% CrO\textsubscript{3}/ZrO\textsubscript{2} samples. Propane oxidative dehydrogenation (ODH) studies reveal that the catalytic activity expressed in molecule of propane converted per gram catalyst per second is similar for the two catalysts, which is consistent with equal amounts of molecularly dispersed chromia present. The turnover frequency for the 6% CrO\textsubscript{3}/ZrO\textsubscript{2} catalyst is, however, smaller than that for the 3% CrO\textsubscript{3}/ZrO\textsubscript{2} sample due to the presence of Cr\textsubscript{2}O\textsubscript{3} crystals, which are relatively inactive for propane ODH. For this catalytic system and for the experimental conditions used, propene, CO, and CO\textsubscript{2} are primary products. Furthermore, the 33–39% propene selectivity is not affected by the C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2} ratio for both catalysts. Structure–reactivity studies suggest that the molecularly dispersed species are present in equal amounts in the 3 and 6% CrO\textsubscript{3}/ZrO\textsubscript{2} samples as Cr\textsuperscript{6+} monochromate and polychromate species which are the most effective catalytic active sites taking part in the propane ODH reaction.

1. Introduction

Oxidative dehydrogenation (ODH) of alkanes provides an attractive alternative for the production of alkenes.\textsuperscript{1,2} Supported transition metal oxides have been extensively used for alkane ODH reactions. For example, vanadia- and molybdena-based catalysts supported on Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2}, SiO\textsubscript{2}, and so forth have been widely studied for alkane ODH reactions.\textsuperscript{3–7} Zirconia (ZrO\textsubscript{2}) has been recently considered as a promising support because of its high thermal and chemical stability.\textsuperscript{6,9} Specifically, the structure–reactivity properties of zirconia-supported vanadia catalysts for the ODH of propane have been studied.\textsuperscript{5,10,11} Chen et al.\textsuperscript{6} studied the influence of loading and catalyst treatment temperature on the structure–reactivity properties of MoO\textsubscript{3}/ZrO\textsubscript{2} catalysts for the ODH of propane. Recently, Gao et al.\textsuperscript{12} studied the influence of the propane/oxygen ratio on the reduction extent of surface V\textsuperscript{5+} cations and the possible effect of reduction extent on the reactivity and selectivity of V\textsubscript{2}O\textsubscript{5}/ZrO\textsubscript{2} catalysts during propane ODH.

Recent studies also reveal that supported chromia systems are also promising catalysts for the propane ODH reaction.\textsuperscript{13–15} De Rossi et al.\textsuperscript{16–18} studied the CrO\textsubscript{3}/ZrO\textsubscript{2}
catalysts for dehydrogenation (DH) of isobutane and propane, reporting that up to monolayer loading the rate of dehydrogenation increases and that the rate of the reaction was also a function of temperature. Furthermore, a mononuclear Cr\(^{3+}\) with two coordination vacancies was proposed as the active species. A comparative study of CrO\(_2\) on Al\(_2\)O\(_3\), SiO\(_2\), and ZrO\(_2\) shows that the turnover frequency (TOF) of the chromia species is high for the zirconia-supported catalyst compared to alumina- and silica-supported catalysts for the range of temperatures studied. Grabowski et al.\(^{19}\) carried out the ODH of isobutane over chromia supported on different oxide supports and observed that the intrinsic activity is high for chromia supported on TiO\(_2\) and ZrO\(_2\) catalysts. This study is, however, limited to a single loading of chromium oxide.

Various characterization techniques have been applied to gain an insight into the nature of the chromium oxide species on zirconia, such as X-ray diffraction (XRD), in situ Raman, Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), electron spin resonance (ESR), and diffuse reflectance spectroscopy (DRS) studies.\(^{20-33}\) Two different types of chromia species were identified under dehydrated conditions by Vuroman et al.\(^{22}\) Based on their Raman and IR spectra, it was suggested that dehydrated alumina-, titania-, and zirconia-supported chromia catalysts possess polymerized chromia species as the major species and distorted tetrahedral monomeric species as a secondary species. The relative ratio of these two different species is essentially independent of chromium oxide loading as the relative intensities and band positions in the Raman and IR spectra are observed to be similar for various loadings.\(^{19,22}\) Isotopic exchange studies using Raman and IR spectroscopy revealed that dehydrated conditions and at higher loadings, surface chromia on zirconia and titania supports are present as isolated or polymeric species.\(^{24,26}\) Studies using ESR spectroscopy revealed the presence of Cr\(^{5+}\) (\(\gamma\)-signal) in CrO\(_3\) on different supports.\(^{23,22}\) These studies reveal that the oxide support—surface chromia interaction stabilizes the Cr species in different oxidation states (Cr\(^{2+}\), Cr\(^{3+}\), Cr\(^{5+}\), and Cr\(^{6+}\)). The relative stability of the different chromia oxidation states depends on the extent of support surface chromia interaction, the acid—base properties of the support, and the interaction energy between the surface chromia and support phases.\(^{34}\)

In the present study, the ODH of propane over CrO\(_2\)/ZrO\(_2\) catalysts is carried out to better comprehend this system. For a better understanding of the CrO\(_2\)/ZrO\(_2\) catalysts, the influence of the propane/oxygen ratio on the reduction of surface Cr cations and the possible effect of reduction extent on the reactivity and selectivity of CrO\(_2\)/ZrO\(_2\) catalysts during propane ODH is studied. Initially two CrO\(_2\)/ZrO\(_2\) catalysts are synthesized by the incipient wetness impregnation technique. These catalysts are characterized by in situ UV—vis—NIR diffuse reflectance and Raman spectroscopy. Finally, the propane ODH reaction was carried out over the two catalysts. Based on the characterization and reaction studies, the structure—reactivity relationships are determined.

### 2. Experimental Section

#### 2.1. Catalyst Preparation

Supported chromia—zirconia catalysts were prepared by the incipient wetness impregnation technique. The precursor used was chromium nitrate nona-hydrate (Cr(NO\(_3\))\(_3\)·9H\(_2\)O), and zirconia (Degussa, 39 m\(^2\)/g) was the support. The pretreated support and incipient volumes of aqueous solutions containing predetermined amounts of the chromium nitrate precursor were intimately mixed in order to prepare catalysts with different loadings of chromium oxide. After the impregnation step, the samples were dried at room temperature and at 110 °C overnight. Finally, the CrO\(_2\)/ZrO\(_2\) samples were calcined at 450 °C for 3 h. The surface coverages were expressed as wt % loading in terms of CrO\(_3\).\(^{25}\)

#### 2.2. Surface Area

The surface areas of the samples were obtained by a multipoint Brunauer—Emmett—Teller (BET) method using N\(_2\) adsorption at 77 K. A Micromeritics Pulse Chemisorb 2700 apparatus was used for this purpose.

#### 2.3. In Situ Raman Spectroscopy

Raman spectra of zirconia-supported chromium oxide catalysts were obtained with a laser Raman apparatus equipped with an argon ion laser (Spectra-Physics, model 165) as the excitation source. The in situ Raman spectrometer system also consisted of a quartz cell with a sample holder, a triple-grating monochromator (Spectraveme, model 1877), and a CCD detector (Jobin Yvon-Spez, ISA Inc., model Spectrum-1). The sample holder was made from a metal alloy (Hastalloy C), and the cap of the sample holder held a 100–200 mg sample. The sample was coated onto a quartz window that was rotated by a 115 V dc motor at a speed of 1000–2000 rpm. A cylindrical heating coil surrounding the quartz cell was used to heat the cell. The quartz cell was capable of operating up to 600 °C, and flowing gas was introduced into the cell at a rate of 50–100 cm\(^3\)/min at atmospheric pressure. The in situ Raman spectra for propane ODH were obtained according to the following procedures. The samples were placed in the cell and heated to 450 °C for 1 h under flowing gas (20% O\(_2\)/He mixture; Scott Specialty Gases, Inc.) and the Raman spectra were recorded. The dehydrated Raman spectra were collected after cooling the samples to 300 °C in a flow of O\(_2\)/He for 30 min. After the above treatment, a C\(_2\)H\(_4\)/He (Scott Specialty Gases, Inc.) and O\(_2\)/He gaseous mixture with varying C\(_2\)H\(_4\)/O\(_2\) ratios was introduced into the cell, and the Raman spectra were collected in situ under reaction temperature at 300 and 400 °C after reaching steady state. Finally, after the propane ODH reaction the samples were reoxidized from 300 to 500 °C under flowing O\(_2\)/H\(_2\) gas and Raman spectra of the samples were recorded.

#### 2.4. In Situ UV—Vis—NIR DRS

The DRS studies of the chromia supported on zirconia catalysts were performed on a Varian Cary 5E UV—vis—NIR spectrophotometer. In situ DRS spectra were taken in the range of 200–800 nm using a Harrick DRS cell (HVC-DR2) with the Prairy Mantis diffuse reflectance spectrometer.
attachment (DRA) to perform the measurements under reaction conditions at elevated temperatures. The samples for the in situ measurements were first calcined in the oven at 450°C for 1 h before immediate transfer to the in situ cell. The reactor in the cell was then pretreated at a sample surface temperature of 400°C in O2/He for 1 h before any further treatment. The dehydrated ZrO2 support at the corresponding reaction temperature was used as the baseline for the supported CrO3/ZrO2 catalysts. Propane ODH with varying C3H8/O2 ratios (1.5 = 1.6C3H8/80O2/40.4He and 3:1 = 9C3H8/30O2/38He) and propane reduction (9C3H8/41He) experiments were performed at different temperatures with a total flow rate of 50 cm3/min. The DR5 spectra were processed with the Bio-Rad WinIR software, by which the Kubelka–Munk function (F(Rs)) is calculated from the absorbance. The edge energy (E0) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of (F(Rs) hv)2 against hv, where hv is the incident photon energy.

2.5. ODH of Propane. The samples were tested for the ODH of propane in a vertical down-flow quartz reactor at atmospheric pressure. The reactor was a single quartz piece with an inlet of 10 mm internal diameter and 15 cm long and an outlet of 5 mm internal diameter and 15 cm long. Two sections were tapered, and the catalyst bed was placed just above the tapered region on quartz wool. The reactor tube was mounted vertically in a tubular furnace. The temperature of the reactor and the catalyst bed was measured by a thermocouple located outside the reactor tube above the catalyst bed and was controlled by a PID temperature controller (FUJ Micro-controller X model PXZ 4). The product gases were sent for online analysis to a gas chromatograph (AIMIL-NUCON 7567) equipped with a methanizer. The carbon oxides and hydrocarbons were analyzed in FID mode using an activated alumina column. The propane and air flow rates were adjusted through separate thermal mass flow controllers (Bronkhost Hi-Tec, model F-201D FAC-22-V) to maintain a specified propane-to-oxygen ratio and a total flow rate of 75 cm3/min. The effect of contact time on propane conversion was studied by changing the reactant flow rate between 50 and 120 cm3/min. A physical mixture of 0.1 g of the catalyst and the required amount of quartz glass powder to form a bed height of 1 cm was loaded into the reactor. Runs were performed at different temperatures, and the reactions were maintained below 5% to ensure minimal surface concentrations that are constant (35-36 m2/g) and are slightly less than that of the pure support, 39 m2/g. Based on the surface areas and chromium oxide loadings of the samples, the Cr surface concentrations (Cr mol/m2) were also determined and are given in Table 1. It is observed that the Cr surface concentration increases with the increase in chromium oxide loading from 8.3 μmol/m2 for the 3% CrO3/ZrO2 sample to 16.9 μmol/m2 for the 6% CrO3/ZrO2 sample. For comparison, Cherian et al. determined the monolayer coverage of chromium oxide on supports to be ~9 μmol/m2.

3. Results and Discussion

3.1. Surface Area and Surface Concentration. The BET surface areas of the pure zirconia support and CrO3/ZrO2 samples were determined and are given in Table 1. The surface area values for the CrO3/ZrO2 samples were relatively constant (35-36 m2/g) and are slightly less than that of the pure support, 39 m2/g. Based on the surface areas and chromium oxide loadings of the samples, the Cr surface concentrations (Cr μmol/m2) were also determined and are given in Table 1. It is observed that the Cr surface concentration increases with the increase in chromium oxide loading from 8.3 μmol/m2 for the 3% CrO3/ZrO2 sample to 16.9 μmol/m2 for the 6% CrO3/ZrO2 sample. For comparison, Cherian et al. determined the monolayer coverage of chromium oxide on supports to be ~9 μmol/m2.

3.2. In Situ Raman Spectroscopy. The Raman spectra of the 3% CrO3/ZrO2 catalyst during propane ODH at 300 °C are shown in Figure 1. The 530, 550, 608, and 625 cm−1 bands in the Raman spectra are due to the monoclinic ZrO2 support. The dehydrated Raman spectrum (b) in Figure 1) is dominated by three Raman bands at 1026, 1000, and 845 cm−1, which were
ZrO₂ catalyst under different conditions reveal that the ZrO₂ sample possesses a Raman band at 932 cm⁻¹ due to the monomeric and polymeric species and disappearance of the band at 932 cm⁻¹ to the monomer and polymeric species. Interestingly, a Raman band under reduction environments and disappears upon reoxidation of the sample. Interestingly, a Raman band at 932 cm⁻¹ is difficult in the Raman spectra due to strong zirconia bands.

Under reducing environments (spectra c–f in Figure 1), the decrease in the intensities of Raman bands at ~1000 and ~845 cm⁻¹ suggests that a reduction of surface polychromate species occurs, whereas the Raman band at 1026 cm⁻¹ is associated with the surface monochromate species is least affected. It can be seen that the band at 1026 cm⁻¹ shifts to 1008 cm⁻¹ and is still present at a reduction temperature of 400 °C. A new Raman band at 932 cm⁻¹ is also observed whose intensity appears to increase with an increase in reduction environment. The presence of a new Raman band at 932 cm⁻¹ suggests that this band is due to a partially reduced chromium oxide species. Reoxidation of the sample at 500 °C (spectrum a in Figure 1) results in the reappearance of the Raman bands due to the mononuclear and polymeric species and disappearance of the band at 932 cm⁻¹. Thus, the extent of reduction of the surface chromium oxide species increases with an increase in reducing environment and the reduced surface chromium species can be restored to its original oxidized form upon reoxidation.

A similar set of experiments was carried out over the 6% CrO₃/ZrO₂ catalyst, and the spectra are shown in Figure 2. In addition to the Raman bands of the surface monochromate and polychromate species, the 6% CrO₃/ZrO₂ possesses a Raman band at ~543 cm⁻¹ due to Cr₂O₃ crystals indicating that the monolayer coverage has been exceeded. Analogous to the above observations for the 3% CrO₃/ZrO₂ sample, the Raman spectra of the 6% CrO₃/ZrO₂ catalyst under different conditions reveal that the extent of reduction of the surface chromium oxide species increases with an increase in C₃H₈/O₂ ratio and the reduced surface chromium species can be restored to its original oxidized form upon reoxidation. Similar to the 3% CrO₃/ZrO₂ sample, a Raman band at ~930 cm⁻¹ is also observed under reduction environments and disappears upon reoxidation of the sample. Interestingly, a Raman band at ~910 cm⁻¹ is observed due to a partially reduced vanadium oxide species on TiO₂ using H₂ as the reducing agent. No significant change is observed in the Raman band intensity at 543 cm⁻¹, suggesting that the Cr₂O₃ crystals are not affected during reaction. Furthermore, comparison of the fully oxidized spectra of the 3 and 6% CrO₃/ZrO₂ catalysts (spectra b in Figures 1 and 2) reveals that the normalized Raman band intensities due to the surface monochromate and polychromate species are similar for the two catalysts. This suggests that the amounts of molecularly dispersed surface monochromate and polychromate species are similar for the two samples. Consequently, the monolayer coverage of chromia on the ZrO₂ support corresponds to 3% CrO₃ and the amount of Cr₂O₃ crystals present in the 6% CrO₃/ZrO₂ corresponds to the additional 3% CrO₃. This is consistent with the monolayer surface concentration of chromia observed on other oxide supports (~9 μmol m⁻²), which is similar to the amount of chromia in the 3% CrO₃/ZrO₂ sample.

3.3. In Situ UV–Vis–NIR DRS. The in situ UV–vis DRS spectra of the CrO₃/ZrO₂ catalysts were obtained at 300 °C under various gas compositions. The spectra in terms of the Kubelka-Munk function versus incident photon energy for the samples under different conditions are shown in Figures 3 and 4 for 3 and 6% CrO₃/ZrO₂, respectively. It can be observed from Figures 3 and 4 that the oxygen ligand to metal charge transfer (LMCT) bands of Cr⁶⁺, located above 3 eV, decrease as the C₃H₈/O₂ ratio increases and are maximum for the pure C₃H₈ in He gas stream, which indicates an increase in the reduction of surface Cr⁶⁺-cations with increasing reducing environments. By using the method developed previously by Gao et al., the relative extents of reduction of the 3 and 6% CrO₃/ZrO₂ catalysts at different gas compositions were determined and are presented in Table 2. Under steady-state reaction conditions at 300 °C, these results indicate

Figure 2. In situ Raman spectra of 6% CrO₃/ZrO₂ at 300 °C in (b) 20% O₂/He; (c) 1.5 = 1.6C₃H₈/80%O₂/40.4He; (d) 3:1 = 9C₃H₈/3O₂/38He; (e) 9C₃H₈/41He; (f) 9C₃H₈/41He/cm³/min at 400 °C; (a) 20% O₂/He at 500 °C.

Figure 3. In situ UV–vis spectra of 3% CrO₃/ZrO₂ at 300 °C in (a) O₂/He; (b) 1.5 = 1.6C₃H₈/80%O₂/40.4He; (c) 3:1 = 9C₃H₈/3O₂/38He; (d) 9C₃H₈/41He cm³/min.)
that the reduction extent of surface Cr\(^{6+}\) increases with the \(\text{C}_3\text{H}_8/\text{O}_2\) ratio and is maximum for the pure \(\text{C}_3\text{H}_8\) in He gas stream. This is consistent with the in situ Raman studies discussed above that the amount of reduced surface chromia species increases with increasing \(\text{C}_3\text{H}_8/\text{O}_2\) ratio. At the same \(\text{C}_3\text{H}_8/\text{O}_2\) ratio and temperature, the relative extent of reduction is more for 3% \(\text{CrO}_3/\text{ZrO}_2\) compared to 6% \(\text{CrO}_3/\text{ZrO}_2\).

Several studies suggest that the edge energies (\(E_g\)) of the LMCT transitions could be very informative in elucidating the local structures of the transitional metal cations, such as \(\text{V}^+\) and \(\text{Mo}^{VI}\). Similar analysis was performed for the present study. The edge energy shifts of the 3 and 6% \(\text{CrO}_3/\text{ZrO}_2\) catalysts during propane oxidation at different gas compositions were measured and are presented in Table 3. It is observed that as the \(\text{C}_3\text{H}_8/\text{O}_2\) ratio increases the edge energy value increases for 3% \(\text{CrO}_3/\text{ZrO}_2\) and is the highest for the pure \(\text{C}_3\text{H}_8\) in He gas stream. Furthermore, the increase in edge energy values for 3% \(\text{CrO}_3/\text{ZrO}_2\) is more than that for the 6% \(\text{CrO}_3/\text{ZrO}_2\) sample. The difference between these increases in edge energy values for the two catalysts appears to be related to the difference in extent of reduction of the two samples. It would appear that a larger amount of reducible surface chromia species is present in the 3% \(\text{CrO}_3/\text{ZrO}_2\) sample compared to the 6% \(\text{CrO}_3/\text{ZrO}_2\) sample; however, the presence of reduced chromia species as \(\text{Cr}_2\text{O}_3\) crystals in the 6% \(\text{CrO}_3/\text{ZrO}_2\) sample may affect the analysis. Under fully oxidized conditions (20% \(\text{O}_2/\text{He}\)), the edge energy shift of 6% \(\text{CrO}_3/\text{ZrO}_2\) is greater than that of 3% \(\text{CrO}_3/\text{ZrO}_2\), due to the presence of \(\text{Cr}_2\text{O}_3\) crystals.

Thus, structural characterization of the two \(\text{CrO}_3/\text{ZrO}_2\) samples suggests that the amount of molecularly dispersed monochromate and polychromate species is similar for the two samples. The monolayer coverage of chromia on this zirconia support corresponds to 3% \(\text{CrO}_3\). Thus, the 6% \(\text{CrO}_3/\text{ZrO}_2\) sample possesses 3% \(\text{CrO}_3\) as molecularly dispersed chromia species and 3% \(\text{Cr}_2\text{O}_3\) as \(\text{Cr}_2\text{O}_3\) crystals. The surface chromia species is reduced under reaction conditions. Of the two types of surface chromia species, the polychromate species is preferentially reduced; however, the monochromate species also undergoes changes under reduced environments considered in this study. Complete reduction of the two species is possible, for example, at 450 °C in butane. \(^{24}\) It appears that a partially reduced surface chromia species is created under reduced environments, which can be reoxidized.

### Table 3. Edge Energy Shifts, \(E_g\) (eV), of the \(\text{CrO}_3/\text{ZrO}_2\) Catalysts for Different Gas Compositions at 300 °C

<table>
<thead>
<tr>
<th>catalyst</th>
<th>(\text{O}_2/\text{He})</th>
<th>(\text{C}_3\text{H}_8/\text{O}_2)</th>
<th>(\text{C}_3\text{H}_8/\text{He})</th>
<th>(\text{C}_3\text{H}_8/\text{He})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% (\text{CrO}_3/\text{ZrO}_2)</td>
<td>3.03</td>
<td>6.44</td>
<td>6.88</td>
<td>7.04</td>
</tr>
<tr>
<td>6% (\text{CrO}_3/\text{ZrO}_2)</td>
<td>3.24</td>
<td>3.32</td>
<td>3.35</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Consequently, the activity is similar and the TOF is smaller for the 6% CrO₃/ZrO₂ sample compared to the 3% CrO₃/ZrO₂ sample. Furthermore, the presence of the Cr₂O₃ crystals in the 6% CrO₃/ZrO₂ sample appears to be in addition to the molecularly dispersed chromia species since the activities are relatively constant and the normalized Raman intensities of the molecularly dispersed species are similar for the two samples.

The relative activity of the surface monochromate and polychromate species is difficult to ascertain based on the present study since the ratio of the two molecularly dispersed species is similar. It is known, however, that the monochromate and polychromate species undergo the oxidation−reduction cycle, a primary requirement for the redox mechanism to occur. The present study reveals that the polychromate species is preferentially reduced though the preferential reduction of a particular species cannot always be used as justification for the higher activity. Previous studies on supported vanadium oxide catalysts using the same ZrO₂ support reveal that preferential reduction of the polyvanadate species occurs. However, the TOF is relatively insensitive to the coverage below monolayer limits though the ratio of the monovanadate and polyvanadate species is a function of vanadia coverage. The main factor involved is the presence of surface V⁵⁺ oxide species. Analogous to the above, it is suggested that the surface monochromate and polychromate species are both active toward propane ODH and the chromia are present as a Cr⁶⁺ species.

The product distribution during propane ODH shown in Table 4 is 33–40% to propene, 48–55% to CO₂, and 10–16% to CO. The propene selectivities for both catalysts are relatively independent of different C₃H₈/O₂ ratios. Additional analysis of the changes in selectivity as a function of temperature, C₃H₈/O₂ ratio, and catalyst reveals that the changes are small and within experimental error. It is tempting, for example, to observe that the propene selectivities, which are slightly higher for the 6% CrO₃/ZrO₂ sample, are due to a decrease in exposed support surface present. Exposed support surface is known to degrade propene. Similar effects have also been observed for the V₂O₅/ZrO₂ system. Thus, the different species present are surface monochromate and polychromate species and crystalline Cr₂O₃. The surface polychromate species are significantly reduced, whereas the monochromate and crystalline Cr₂O₃ species are not significantly affected during the ODH reaction. It appears that the surface monochromate and polychromate species are both active for the propane ODH reaction.

### 4. Conclusions

Two supported chromia catalysts were prepared by the incipient wetness impregnation method on a ZrO₂ support. The calcined samples were characterized by in situ UV−vis−NIR diffuse reflectance and Raman spectroscopic techniques. The dehydrated Raman spectra revealed that the 3 and 6% CrO₃/ZrO₂ catalysts possess an equal amount of molecularly dispersed monochromate and polychromate species. Thus, the monolayer coverage for this CrO₃/ZrO₂ system corresponds to about 3% CrO₃. The 6% CrO₃/ZrO₂ catalyst possesses additional Cr₂O₃ crystals corresponding to the remaining 3% CrO₃. The in situ UV−vis−NIR DRS and Raman spectroscopic studies of the CrO₃/ZrO₂ catalysts during propane ODH indicate that the surface Cr⁶⁺ sites were reduced under steady-state reaction conditions depending on the reduction environment (propane/O₂ ratio) and surface chromia loading. Furthermore, it appears that the surface polychromate species was preferentially reduced compared to the surface monochromate species. The in situ Raman spectra reveal that a new reduced chromia species was formed during reduction that can be readily oxidized. The reactivity studies suggest that the activity was similar for the two

### Table 4. Catalytic Results of Propane ODH over the Supported CrO₃/ZrO₂ Catalysts

<table>
<thead>
<tr>
<th>Catalyst (weight, g)</th>
<th>Reaction Temperature (°C)</th>
<th>C₃H₈/O₂ Ratio</th>
<th>Activity, A₇ (mol/g·s) × 10⁶</th>
<th>TOF (s⁻¹) × 10³</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% CrO₃/ZrO₂ (0.02)</td>
<td>360</td>
<td>2:1</td>
<td>0.53</td>
<td>1.76</td>
<td>34 50 16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:1</td>
<td>0.54</td>
<td>1.80</td>
<td>33 52 15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4:1</td>
<td>0.46</td>
<td>1.54</td>
<td>34 52 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1</td>
<td>0.92</td>
<td>3.1</td>
<td>34 54 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:1</td>
<td>0.99</td>
<td>3.3</td>
<td>33 55 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4:1</td>
<td>1.15</td>
<td>3.8</td>
<td>34 54 12</td>
</tr>
<tr>
<td>6% CrO₃/ZrO₂ (0.025)</td>
<td>360</td>
<td>2:1</td>
<td>0.51</td>
<td>0.85</td>
<td>39 48 13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:1</td>
<td>0.53</td>
<td>0.88</td>
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Figure 5. Variation of propane conversion (solid symbols) and selectivity (open symbols) with W/F for 3% CrO₃/ZrO₂ during ODH of propane at 380 °C, C₃H₈/O₂ = 3:1.
samples since the same amounts of molecularly dispersed chromia species are present. Consequently, the TOF based on the total surface chromium oxide species is greater for the 3% CrO₃/ZrO₂ compared to the 6% CrO₃/ZrO₂ catalyst. For both catalysts, it appears that propene, CO, and CO₂ were primary products since the selectivities were invariant with contact time. Furthermore, no significant changes in propene selectivities occur with changes in the C₃H₈/O₂ ratios used. Thus, the structure-reactivity relationship of the CrO₃/ZrO₂ system depends on the nature of the chromium oxide species present: the polychromate species that are preferentially reduced and the monochromate species and Cr₂O₃ crystals that are not significantly affected during propane ODH. The surface monochromate and polychromate species, however, appear to be the catalytic active sites for propane ODH.

Acknowledgment. Two of the authors (T.V.M.R. and G.D.) are grateful to the Ministry of Human Resources and Development (MHRD) for partial support of the work carried out at IIT Kanpur. The Division of Basic Energy Sciences, Department of Energy, under Grant DEF02-93ER14350, is gratefully acknowledged for the work carried out at Lehigh University.