

## In Situ Ultraviolet Raman Spectroscopy of the Reduction of Chromia on Alumina Catalysts

Vivian S. Sullivan,<sup>†</sup> S. David Jackson,<sup>‡</sup> and Peter C. Stair\*,<sup>§</sup>

Argonne National Laboratory, Argonne, Illinois 60439, Department of Chemistry, Joseph Black Building, The University, Glasgow G12 8QQ, Scotland, UK, and Department of Chemistry and Centre for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208

Received: July 29, 2004; In Final Form: October 18, 2004

A fluidized bed in situ cell is used to examine the chromia on alumina catalyst surface. The loading is varied from 1 to 20% chromium oxide on alumina. The structure of the surface is monitored as a function of temperature, reduction, and hydration. This is the first study to use ultraviolet excitation to study a reduced chromium catalyst surface. Reduction of the sample in hydrogen gas leads to the formation of noncrystalline  $\text{Cr}^{3+}$  species. Addition of potassium to the surface reduces the size of the chromia clusters.

## Introduction

The characterization of the surface of supported metal oxide catalysts is vital to the understanding of many catalytic reactions. Supported chromium oxide catalysts are used for many industrial catalytic processes.<sup>1</sup> Chromium oxide supported on alumina is used as a catalyst for propane and butane dehydrogenation.<sup>2–11</sup> Determination of the surface structure under reaction conditions is important for a complete understanding of the catalyst system.

Raman spectroscopy is a powerful technique for characterization of solids and surfaces and is well-suited for examining oxides and supported oxide catalysts.<sup>12–18</sup> Raman spectroscopy has been used to characterize the surface of supported chromium oxides.<sup>1,19–26</sup> These studies have looked at hydrated and dehydrated surfaces of chromium oxide on alumina, titania, and silica at loadings of 0.2–30%. The use of UV excitation prevents fluorescence from the Raman spectra by exciting the sample at a frequency where fluorescence does not occur.<sup>27,28</sup> It may also increase the Raman intensity of some vibrational bands due to resonance enhancement. Over the past few years, our group successfully examined a number of catalytic systems using UV Raman spectroscopy.<sup>2,29–34</sup> A method has been developed in our laboratory for collecting UV Raman spectra of solids, including catalysts, which minimizes sample heating or degradation. A “fluidized bed” sample cell<sup>34</sup> uses a combination of gas flow and mechanical shaking to produce a flowing bed of sample particles. This minimizes the exposure to the laser for each individual location on the surface and reduces the contribution of sample damage to the measured spectrum. Previous studies of supported chromia species<sup>20,22</sup> demonstrate that surface dehydration of supported chromium oxides due to laser heating can obscure the identification of species that are hydrated prior to exposure to the laser beam.

The focus of the present study is a series of chromium oxide catalysts supported on alumina that are active for the dehydrogenation of propane to propene. Catalytic dehydrogenation of light alkanes with catalysts based on platinum or chromium oxides on alumina is an established technology.<sup>35</sup> Catalyst deactivation by carbon deposition is a significant problem.

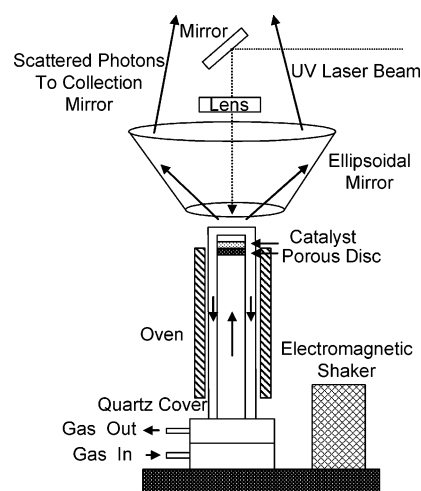


Figure 1. Schematic diagram of the in situ fluidized bed reactor.

Regular regeneration of the catalysts is required to sustain activity of the catalyst.<sup>35</sup> Determination of the surface structure of chromium oxide on alumina allows an understanding of the nature of the active surface species, which could allow optimization of catalysts and possible reduction of side reactions leading to coke formation. We have used the fluidized bed in situ cell to examine the surface under reducing and oxidizing conditions and determine the surface structure as a function of temperature and chromium oxide loading.

## Experimental Section

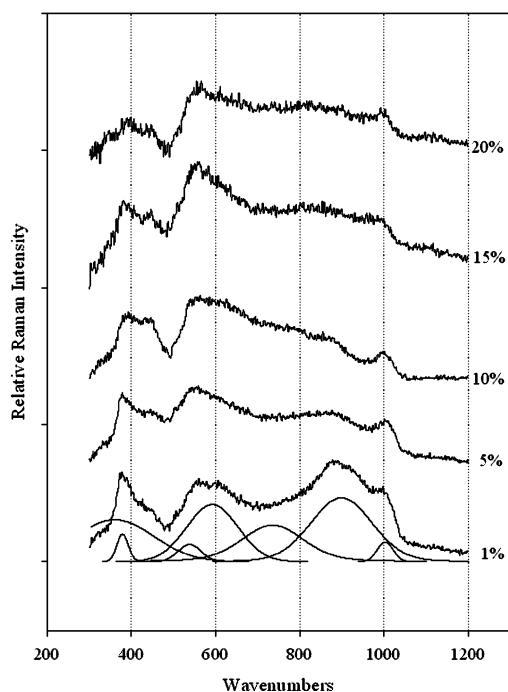
A schematic diagram of the in situ fluidized bed sample cell is shown in Figure 1 and is described in detail in an earlier paper by Chua and Stair.<sup>34</sup> A stainless steel, porous disk with 40- $\mu\text{m}$ -diameter pores is secured near the top of a stainless steel tube. The sample is placed on the porous disk, and gas is introduced into the cell, flowing up the tube and through the porous disk. A quartz cover is used to surround the tube when a controlled environment is necessary. A cylindrical furnace surrounds the cell and is used to maintain high temperatures during collection of the Raman spectra. An electromagnetic shaker is attached to the base of the cell to facilitate tumbling

\* Corresponding author. E-mail: pstair@northwestern.edu.

<sup>†</sup> Argonne National Laboratory.

<sup>‡</sup> The University, Glasgow.

<sup>§</sup> Northwestern University.



**Figure 2.** Dehydrated surface spectra of 1, 5, 10, 15, and 20% chromium oxide on alumina.

of the catalyst particles. The temperature is measured using a thermocouple centered below the fritted disk supporting the sample.

The laser beam is focused down onto the top surface of the sample bed and an ellipsoidal mirror collects the scattered photons. The sample is either a fluidized powder covering the porous disk or a pressed pellet with a diameter much smaller than the disk. The ambient atmosphere at the point of collection for the Raman spectra in both cases is the gas specified in the discussion or ambient atmosphere if no gas is specified. The UV Raman instrument is a Spex 1877 triple grating spectrometer with an imaging multichannel photomultiplier tube (IMPT) detector. The laser source is a Lexcel 95 SHG argon ion laser with an intracavity nonlinear crystal, BBO ( $\beta$ -barium borate,  $\text{BaB}_2\text{O}_4$ ), that frequency doubles visible radiation into the mid-ultraviolet. The 488-nm line doubled to 244 nm was used for all spectra in this study. The power delivered to the samples was between 0.8 and 30 mW. Spectral collection times varied from 0.5 to 15 h, and the longer collection times were used for the fluidized samples.

Catalyst samples were prepared and provided by Johnson-Matthey (formerly Syntex). A solution of ammonium dichromate or potassium hydroxide and ammonium dichromate was added to the support (Engelhard Al-3992E, S. A.  $200 \text{ m}^2 \text{ g}^{-1}$ ) and the resulting suspension evaporated to dryness. The solid was then calcined in air at 823 K for 3 h. The weight percent loadings of  $\text{Cr}_2\text{O}_3$  are 1, 5, 9, 10, 15, and 20%. The 1% catalyst is yellow, and the 5% sample is orange. The 10, 15, and 20% catalysts are brown, with the higher loadings being a darker brown. X-ray diffraction following calcinations showed  $\gamma\text{-Al}_2\text{O}_3$  as the only crystalline material. A sample composed of 9%  $\text{Cr}_2\text{O}_3$  with 1%  $\text{K}_2\text{O}$  supported on alumina was also examined. Stationary samples are pellets pressed at 2 tons, and fluidized samples are a powder composed of 90  $\mu\text{m}$  diameter spheres.

## Results

**Catalyst Surface Structure.** Figure 2 shows the UV Raman spectra of stationary catalysts, formed into pellets, measured in

air. On the basis of previous studies, the supported chromia species are likely to be hydrated prior to exposure to the laser beam and then dehydrated under these stationary sample conditions. Surface dehydration of supported chromium oxides due to laser heating of the samples has been demonstrated in previous studies.<sup>20,22</sup> In the region below  $500 \text{ cm}^{-1}$ , three bands are seen in the spectra at 360, 390, and  $450 \text{ cm}^{-1}$ . The band at  $360 \text{ cm}^{-1}$  dominates at 1 and 5% loadings. The bands at 390 and  $450 \text{ cm}^{-1}$  increase in intensity with higher loadings. Above  $500 \text{ cm}^{-1}$ , with 1% chromium loading, a band at  $900 \text{ cm}^{-1}$  dominates the spectrum. This band broadens with increased loading of chromium oxide. In addition, the spectral intensity between 550 and  $800 \text{ cm}^{-1}$  increases relative to the bands at 900 and  $360\text{--}450 \text{ cm}^{-1}$ .

The spectral intensity in the region  $550\text{--}800 \text{ cm}^{-1}$  is resolved into three peaks at 550, 600, and  $720 \text{ cm}^{-1}$  by curve-fitting. This is the minimum number of peaks required to provide an adequate fit to the measured spectrum. The assignments of the bands are based on known literature values of chromium oxide surface species; a sample fit is shown for the 1% loading. Monomeric, dimeric, trimeric, and polymeric chromium oxides as well as the crystalline species  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  and noncrystalline  $\text{Cr}_2\text{O}_3$  are considered in analyzing the spectra. Surface bonding via  $\text{Al}\text{--O}\text{--Cr}$  linkages is also a contribution to the spectrum. Some bands seen in the dehydrated sample spectra cannot be assigned to only one species.

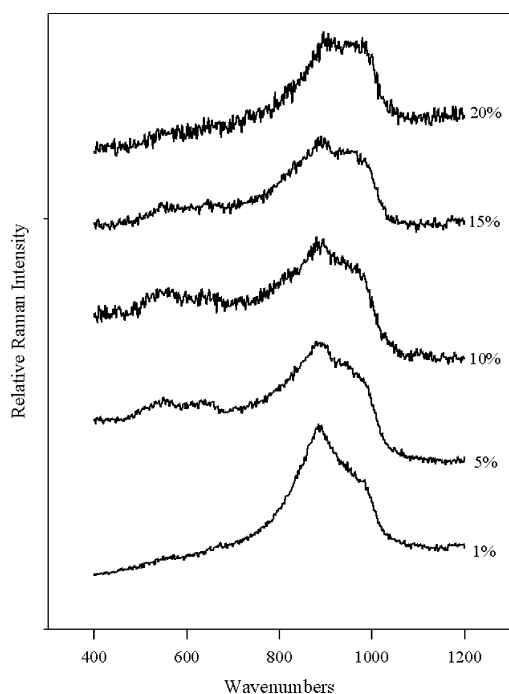
In the lower wavenumber region of the stationary catalyst spectra, bands are seen at 360 and  $390 \text{ cm}^{-1}$ , the former is attributable to contributions from both monomeric and dimeric chromium oxide<sup>19,20,22,23,36</sup> and the latter to polymeric chromium oxide.<sup>24,36</sup> Other polymer bands from bridging  $\text{Cr}\text{--O}\text{--Cr}$  bonds have been identified previously at 550, 600, and  $720 \text{ cm}^{-1}$ .<sup>24,36,37</sup> On the basis of a study of supported vanadium oxide,<sup>38</sup> the band around  $900 \text{ cm}^{-1}$  is assigned to  $\text{Cr}\text{--O}\text{--Al}$  vibrations. An alternate assignment of the band around  $900 \text{ cm}^{-1}$  is  $\text{Cr}\text{--O}\text{--Cr}$  vibrations of monomeric, dimeric, trimeric, and polymeric chromium oxides.<sup>19,20,22,23,36</sup>

The intensity of the monomer/dimer band,  $\sim 360 \text{ cm}^{-1}$ , relative to the polymer band,  $\sim 390 \text{ cm}^{-1}$ , is large for both the 1 and 5% catalysts. For the 10% catalyst, the intensity of the monomer band is similar to the polymer band. The 15 and 20% catalysts have very similar spectra. At these high loadings the contributions to the spectra from the monomer/dimer band are very small relative to the  $390\text{-cm}^{-1}$  polymer band.

As the loading of chromium oxide increases, the contribution of the  $\text{Cr}\text{--O}\text{--Al}$  band around  $900 \text{ cm}^{-1}$  decreases relative to the  $\text{Cr}\text{--O}\text{--Cr}$  bands. The  $\text{Cr}\text{--O}\text{--Cr}$  bridging bonds gain in intensity with loading. A  $\text{Cr}\text{=O}$  band at  $1000 \text{ cm}^{-1}$  is strong in all of the spectra. The presence of this band is taken as an indication of dehydration. Monomeric and dimeric chromium oxide species are transformed into polymeric form upon dehydration.

For all loadings a band is seen at  $450 \text{ cm}^{-1}$  that is assigned to noncrystalline  $\text{Cr}_2\text{O}_3$ . This assignment is discussed in detail below. The presence of  $\text{Cr}^{3+}$  is not unexpected, as calcination in air at elevated temperatures has been seen to lead to a small amount of reduction of the chromium.<sup>20,22,39–41</sup> Crystalline  $\text{CrO}_3$  has a band at  $500 \text{ cm}^{-1}$ <sup>20–22,36</sup> and crystalline  $\text{Cr}_2\text{O}_3$  has a single band at  $550 \text{ cm}^{-1}$ ;<sup>19,23,36,42</sup> these bands are not present in the catalyst spectra at any loading. The band seen in the spectra at  $550 \text{ cm}^{-1}$  is assigned to polymeric species ( $\text{Cr}\text{--O}\text{--Cr}$  stretch), as was seen in a recent paper.<sup>37</sup>

To examine the catalyst surface without dehydration by the UV laser, the chromium oxide surface species were also



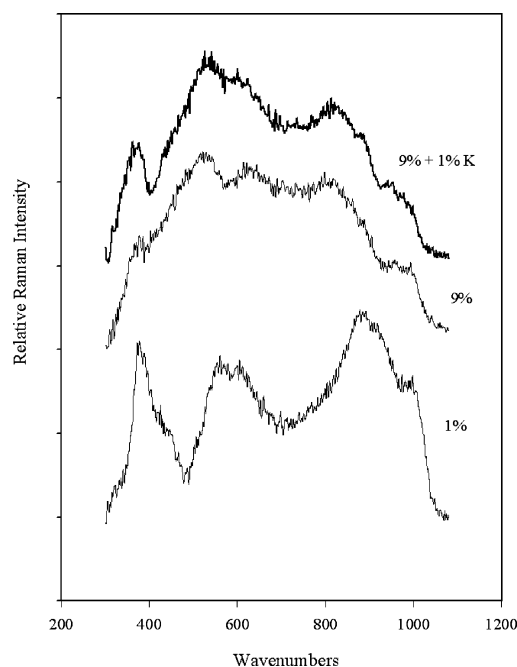
**Figure 3.** Hydrated surface spectra of 1, 5, 10, 15, and 20% chromium oxide on alumina.

examined using the fluidized bed sample cell, which tumbles the catalyst particles and minimizes laser heating and photochemistry.<sup>34</sup> UV Raman spectra of the catalyst surfaces, collected using the fluidized bed, are shown in Figure 3. The main band in the spectra is seen at  $900\text{ cm}^{-1}$ , which broadens with increased loading of chromium oxide. A band is also seen at  $550\text{ cm}^{-1}$  for all spectra except the 1% chromium oxide catalyst.

The fluidized bed spectra are quite different from that of the stationary catalyst. The 1% chromium oxide sample shows no contributions from chromium oxide cluster species. Small contributions from the cross-linked chromium oxide species appear in the spectra for the 5% catalyst at  $550\text{ cm}^{-1}$ . In comparison with the spectra of the stationary catalyst, the amount of Cr–O–Cr bonding is very small. Contributions from the cross-linked chromium oxide species also appear in the spectra for the hydrated surface of the 10, 15, and 20% catalyst. The Cr–O–Cr bands do not change appreciably with loading. At all chromium loadings the spectrum is dominated by the Cr–O–Al surface band around  $900\text{ cm}^{-1}$ . The band between 900 and  $1000\text{ cm}^{-1}$  broadens with increasing loading, which is likely due to a change in the Cr–O–Al bonding.<sup>38</sup> In these samples we have a mixture of species with differing degrees of hydration at all loadings. The proportions of various chromium oxide bonds will change with loading, which leads to changes in the Raman spectra.

While the catalyst surface is not dehydrated by the laser, polymeric chromium oxide species are still seen on the catalyst surface, indicating that the catalyst surface is not fully hydrated, even after exposure to air after calcination. The relative contribution of the band arising from the interaction of the chromium oxide with the alumina support is stronger in the fluidized bed spectra than in the stationary spectra. The degree of dehydration and polymerization is expected to be greater in the stationary spectra where laser dehydration is a factor.

**Effect of Potassium Additives.** When potassium is added to the catalyst, the formation of coke is retarded.<sup>2,9</sup> The surface structure of the chromium oxide is modified by the addition of

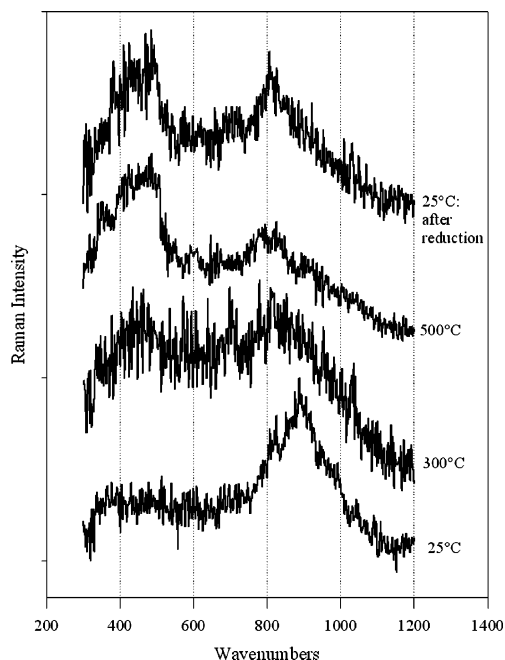


**Figure 4.** Spectra of 9% chromium oxide on alumina with and without 1% potassium; that of 1% chromium oxide on alumina shown for comparison.

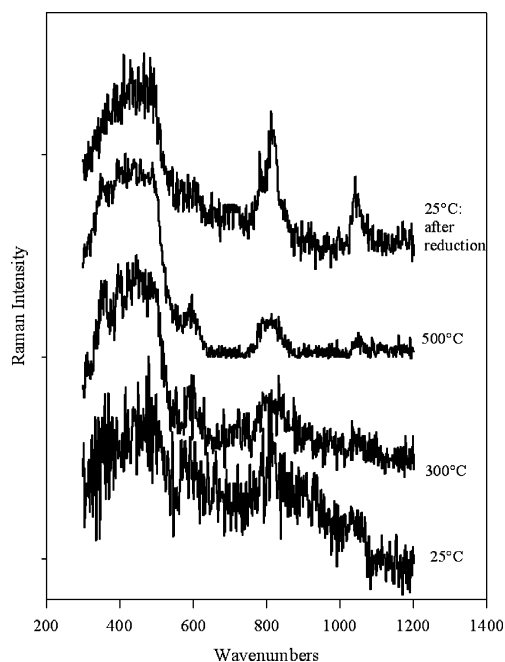
1% K to the catalyst (Figure 4). The differences in the spectra of 9% chromium oxide on alumina with and without 1% K are seen to be minor in comparison with the differences produced by changes in the loading (compare the 1% chromium oxide spectrum). However, the band at  $360\text{ cm}^{-1}$  in the 1% chromium oxide spectra is enhanced in the 9% spectrum with addition of 1% K. This band is assigned to the monomeric and dimeric chromium oxide species. The effect of K is to reduce the amount of polymerization, possibly by replacing hydrogen in hydroxyl groups. The reduction in degree of polymerization suggests a larger population of smaller chromia clusters. This result is consistent with the earlier study showing that addition of  $\text{K}_2\text{O}$  to the catalyst did not have any measurable electronic effect on the chromium oxide species, since the polymeric and monomeric chromium species are both  $\text{Cr}^{6+}$ .<sup>2</sup>

**Reduction and Oxidation.** Hydrogen gas was used to reduce the sample, simulating the reduction of the sample under reaction conditions without spectral interference from propane, propene, or coke formation. Dehydration of some supported chromium oxide catalysts has been shown to occur with heating.<sup>1,20,22</sup> Our samples changed color from yellow (1%) and brown (20%) to green, which indicates the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ . After extraction of all  $\text{Cr}^{6+}$  from the surface of the reduced sample with HCl,<sup>41</sup> the green color remains, confirming that the species is  $\text{Cr}^{3+}$ . Both blue and green samples have been obtained in previous experiments for chromium oxide supported on silica by varying the reaction conditions.<sup>43</sup> Green samples have been described as  $\text{Cr}^{3+}$  in noncrystalline three-dimensional clusters.<sup>43</sup>

Spectra measured during the reduction of 1 and 20% chromium oxide catalysts are shown in Figures 5 and 6, respectively. The fluidized bed sample cell was used to perform the reduction and minimize laser-induced photochemistry; pure hydrogen was used as the fluidizing gas. A broad band is formed upon reduction of both 1 and 20% loadings, at approximately  $450\text{ cm}^{-1}$ , and a decrease in the Cr–O–Al surface interaction band is seen. The frequency of the new band is too low to be pure crystalline  $\text{Cr}_2\text{O}_3$ ,<sup>19,23,36,42,44</sup> and it may be due to an amorphous  $\text{Cr}^{3+}$  species, such as  $\text{Cr}(\text{OH})_3$ <sup>44</sup> or noncrystalline



**Figure 5.** Fluidized bed Raman spectra of 1% chromium oxide on alumina, reduced in hydrogen, as a function of temperature.



**Figure 6.** Fluidized bed Raman spectra of 20% chromium oxide on alumina, reduced in hydrogen, as a function of temperature.

$\text{Cr}_2\text{O}_3$  in three-dimensional clusters.<sup>43</sup> The  $450\text{ cm}^{-1}$  band is present even after initial exposure to hydrogen at room temperature for the 20% sample. This  $\text{Cr}^{3+}$  species is stable in a reducing atmosphere, remaining present in the spectra when the samples are cooled in hydrogen. A small amount of  $\text{Cr}_2\text{O}_3$ , at  $550\text{ cm}^{-1}$ , is seen in the 20% spectra. The sharp bands at  $800$  and  $1050\text{ cm}^{-1}$  are pure rotational Raman bands from the  $\text{H}_2$  gas. Exposure to oxygen reverses the reduction.

In other experiments the UV laser was observed to change the surface structure even at high temperatures in ambient hydrogen. Examination of the spectra of 1% chromium oxide as a stationary pellet at  $500^\circ\text{C}$  shows only  $\text{Cr}^{6+}$  in the stationary catalyst spectra, even though, overall, the catalyst color is green, indicating the presence of  $\text{Cr}^{3+}$ . The laser heating at a single

spot appears to be changing the structure of the surface; spectra were also collected where  $\text{Cr}^{6+}$  was removed from the catalyst with HCl, but when Raman spectra were collected, laser heating caused oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  at room temperature. Previous studies have shown that  $\text{Cr}^{3+}$  can be oxidized to  $\text{Cr}^{6+}$  by heating.<sup>41</sup>

## Discussion

The catalysts examined in this study show a greater degree of dehydration on the surface than was seen in earlier studies, even using the fluidized bed cell. Differences in preparation or calcination may account for this difference. In this study, we have found the proportion of  $\text{Cr}-\text{O}-\text{Cr}$  bonded compounds of  $\text{Cr}^{6+}$  increases with increasing chromium oxide loading in samples at room temperature. When chromium oxide on alumina catalysts are prepared, only  $\text{Cr}^{6+}$  is present on the surface before calcination.<sup>39</sup> After calcination above  $500^\circ\text{C}$ ,  $\text{Cr}^{3+}$  is formed due to calcination-induced reduction of  $\text{Cr}^{6+}$ . The compound used to prepare the catalysts does not have an effect on the resulting proportion of  $\text{Cr}^{6+}$  ions.<sup>41</sup> Two forms of  $\text{Cr}^{6+}$  have been found on supported chromium oxide catalyst surfaces,<sup>1</sup> an easily reducible polychromate species and a monochromate species that is harder to reduce.

For the laser dehydrated stationary samples, the catalysts with 1 and 5% chromium oxide loading have relatively large concentrations of monomeric and dimeric chromium oxide species. As the loading of chromium oxide is increased, the contribution of the  $\text{Cr}-\text{O}-\text{Cr}$  bridging bands to the spectra is increased. The change in the relative amount of surface bonding as compared to the amount of chromium–chromium bonding indicates the formation of larger clusters. No crystalline  $\text{CrO}_3$  or  $\text{Cr}_2\text{O}_3$  is detectable at any loading by Raman or XRD (not shown), in contrast to previous reports.<sup>23</sup> This result is likely due a change in the composition of the impregnation solution and a shorter calcination time.  $\text{Cr}^{3+}$  is present with a band at  $450\text{ cm}^{-1}$  for all chromium oxide loadings.

The fluidized bed samples have only a small amount of cross-linked chromium oxide present on the surface. The 1% sample shows no signs of  $\text{Cr}-\text{O}-\text{Cr}$  bonding. The 5, 10, 15 and 20% samples all have cross-linked chromium oxide on the surface, but the  $\text{Cr}-\text{O}-\text{Al}$  surface bonds dominate the spectra. These samples are not dehydrated by the exposure to the laser and are partially hydrated by water in the air after calcination.

For both 1 and 20% chromium oxide loadings, the  $\text{Cr}^{3+}$  bands dominate the spectrum upon heating in a reducing atmosphere. Dehydrogenation of propane and butane by the chromia catalyst produces reducing conditions at the catalyst surface. Therefore, the spectra of the catalyst surface under hydrogen are most likely to represent the catalyst under reaction conditions. Noncrystalline  $\text{Cr}^{3+}$  is formed upon reduction of the dispersed  $\text{Cr}^{6+}$  in hydrogen; crystalline  $\text{Cr}_2\text{O}_3$  is not formed and cannot be the active catalytic site. The proposed active site for propane dehydrogenation over chromium oxide on alumina is  $\text{Cr}^{3+}$ .<sup>10,11,45</sup> The active form of the chromia is assumed to be mononuclear due to a linear dependence of the dehydrogenation rate on the chromium concentration over a concentration range from 0.078 to 1.55% chromium.<sup>10,45</sup>

All of the spectra in this study were collected using UV excitation. Previous studies have shown that the choice of wavelength used for the Raman spectroscopy can have a large effect on the measured spectra.<sup>37,38</sup> In previous studies of supported chromium oxides,<sup>37</sup> the lower wavenumber bands are enhanced relative to the bands between  $850$  and  $1000\text{ cm}^{-1}$ . Our spectra show a similar intensity pattern, so the chromium



oxide cluster bands are enhanced relative to the surface interaction bands by the resonance Raman effect of the UV excitation.

## Conclusion

Reduction of the sample in H<sub>2</sub> leads to the formation of noncrystalline Cr<sup>3+</sup> species. Addition of K, which reduces coking under reaction conditions, reduces the size of the chromium oxide clusters on the catalyst surface. This suggests that controlling the state of chromium dispersion is an important factor in developing a coke-resistant catalyst. Increased loading of Cr<sub>2</sub>O<sub>3</sub> on the alumina leads to higher levels of Cr—O—Cr bonding and a relative reduction in the amount of chromium oxide to surface bonding. Laser dehydration of the surface promotes formation of chromium oxide clusters on the catalyst surface.

These results demonstrate the value of the fluidized bed sample configuration for accurate determination of the surface structure of supported oxide catalysts. Dehydration of the surface by laser-induced heating leads to polymerization of surface metal oxides, obscuring the true surface structure. Even at temperatures high enough to cause a degree of surface dehydration, the effect of the laser heating and photochemistry is important and prevents accurate measurement of the reduced surface conformation.

**Acknowledgment.** This research was funded by The Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy, under Grant DE-FG02-97ER14789. Samples were provided by Syntex (ICI).

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