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# Catalytic Conversion of Alcohols. Relation of Hafnium-Zirconium Mixed Oxide Catalytic Selectivity to Surface Composition Measured by Raman Spectroscopic Methods

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The Raman spectra obtained for a series of mixed Hf-Zr oxide catalysts, prepared by coprecipitation, indicate that the surface composition is similar to the bulk composition. Hf, impregnated on calcined zirconia, remains on the surface following calcination at 600 °C but migrates into the bulk if calcination is effected at 1000 °C. The catalytic selectivity abruptly changes from that of pure hafnia to that of pure zirconia at a composition corresponding to Hf:Zr = ca. 1:9 rather than that undergoing a gradual change that follows the surface composition. Surface Hf may produce a significant background in the Raman spectra that increases for higher Hf compositions; the extent of the background depends upon both calcination temperature and Hf composition.

## Introduction

The role of the geometrical arrangement of surface atoms has been an active area of research in heterogeneous catalysis since the geometric factor was advanced by Balandin[1] more than 50 years ago. The role of electronic factors in determining catalytic activity was emphasized in the 1940-1950 period. Even though many workers realized that the geometric and electronic factors were not independent, many useful experiments were designed by considering them to be independent (e.g., Dowden[2] and Beeck[3]). Ponec,[4] in fact, considers the 1950 papers by Dowden and Beeck as probably the most stimulating on catalysis in the whole postwar period.

Evaluating the role of surface or bulk properties upon catalytic characteristics is more realistic than concentrating upon geometric or electronic properties. Essentially all studies directed toward differentiating between the role of surface and bulk properties have utilized metal alloy catalysts. For example, Sachtler and van der Plank[5] wrote "From recent results on the hydrogen chemisorption by copper-nickel alloys and their catalytic activity in hydrogenating benzene it follows that chemisorption and catalysis are not determined by collective properties of the catalyst such as filing of its d-band, but by the chemical properties of the individual surface atoms". On the other hand, Sinfelt introduced the term "bimetallic clusters" to refer to highly dispersed bimetallic entities present on the high surface area carriers where, in some cases, combinations of metals that are immiscible in the bulk have catalytic properties that are not those expected from the two metals acting independently.[6]

Freeman et al.[7] noted that the olefin selectivity for 2-octanol dehydration by zirconia differed greatly from that of hafnia. The factors important in preparing stable, homogeneous bulk metal oxide solid solutions—valence, ionic size, crystal structure, heat of formation, solubility, etc.—are nearly identical for hafnia and zirconia. It was observed that the olefin selectivity for 2-octanol dehydration underwent an abrupt change from that of hafnia to that of zirconia at a solid solution composition of about 0.8 Zr (Figure 1) rather than that of a continuous change in selectivity that paralleled the bulk composition change. Furthermore, pure zirconia impregnated to produce a "surface mixed oxide" showed a selectivity pattern that resembled that of the bulk solid solution catalysts (Figure 1). Surface analytical instruments (ESCA, AES, and ISS) were utilized to establish surface compositions for the various catalysts. The results from ESCA and ISS measurements were consistent with all of the mixed oxides having the same bulk and surface compositions.[8] Surface area and crystallite size (XRD line broadening and TEM) did not parallel the abrupt catalytic selectivity change.

Surface composition is difficult to establish and additional analyses are needed to show that olefin selectivity changes abruptly while, at the same time, the surface and bulk compositions exhibit a monotonous variation. The most intense Raman band position for the monoclinic phases of hafnia and zirconia differ by about 28 $cm^{-1}$ and, furthermore, this band position is linearly related to the composition of the hafnium-zirconium dioxide solid solution.[9] Therefore, it appeared that the Raman band position could provide further evidence to substantiate the ref 8 surface characterization studies. This report describes Raman spectroscopic experiments designed to determine the composition of the hafnium-zirconium oxide catalysts utilized in alcohol dehydration studies.[8]

## Experimental Section

*Bulk Oxides.* Zirconia was prepared by rapidly dumping excess concentrated ammonium hydroxide into a vigorously stirred ca. 0.3 M aqueous zirconyl nitrate solution; this preparative procedure produces primarily monoclinic zirconia following 600 °C calcination of the washed precipitate.[10]

Hafnium metal (97 or 99.9% Hf) was first dissolved in aqueous hydrofluoric acid and then ammonium hydroxide was added to effect precipitation of the hydrous oxide. The gel was washed five times by repeated dispersion and filtration steps. The washed gel was then dissolved in concentrated nitric acid and then an amount of this Hf solution was added to a zirconyl nitrate solution to provide the appropriate Hf-Zr concentration. A mixed metal gel was prepared by precipitation by adding concentrated ammonia. The mixed metal gel was dried and calcined as outlined above, and as described in ref 10 for pure $ZrO_2$.

*Surface Hafnium-Zirconium Oxides.* Monoclinic zirconia was prepared by calcining a dried zirconia gel at 600 °C. This calcined material was impregnated with an appropriate portion of the hafnium nitrate solution prepared as described above. The amount of hafnium required to give the desired surface coverage was calculated assuming that $HfO_2$ occupied an area that corresponds

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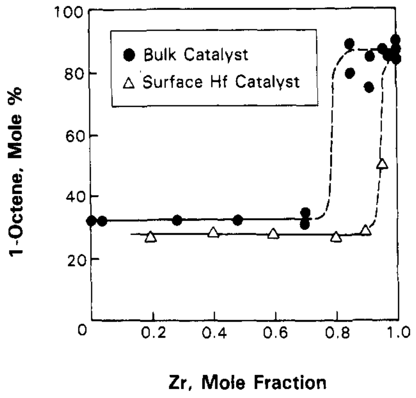

**Figure 1.** The fraction of 1-octene present in 2-octanol dehydration products using bulk hafnia-zirconia (●) or hafnia surface impregnated zirconia (▲) catalysts at 250 °C and 1 atm alcohol pressure.

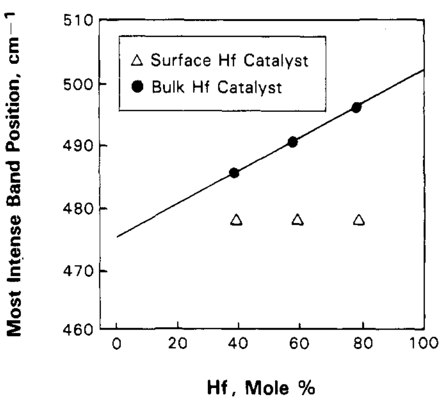

**Figure 2.** Position for the most intense Raman band for the monoclinic phase for coprecipitated hafnia-zirconia samples (●) and hafnia surface impregnated zirconia samples (△) following calcination at 1000 °C (solid line represents data from ref 9 for samples calcined at 1400 °C).

to the area projected onto a base plane of the $HfO_2$ unit cell. The impregnated material was dried at 120 °C and then calcined at 600 °C in air.

*Raman Spectra.* Samples were irradiated by a Spectra Physics Model 164 argon ion laser operating at 514.5 nm. A Spex Model 1403 double monochromator equipped with a CD2 compudrive system and a Hewlett-Packard 7090A plotting system was used to record spectra. The photon detection system consisted of a cooled RCA 31034 photomultiplier coupled to an ORTEC photon-counting system. Samples were placed in a capillary melting point tube. The spectral band-pass was 6 $cm^{-1}$.

*Alcohol Conversion.* The catalyst, in a plug flow reactor, was treated in flowing hydrogen at 500 °C for 4 h prior to use. Alcohol was pumped over the catalyst at ca. 0.4 LHSV. Liquid products were collected at intervals and analyzed for conversion and alkene distribution using gas chromatography.[8] A normal catalytic run lasted for 5–8 h with samples being collected at approximately hourly intervals. Apart from a slight (usually 20–30% of original activity) decline in activity the product compositions were similar throughtout a run period. Conversion levels varied between about 2 and 20% of the alcohol changed; a mixed oxide containing approximately 20% Hf appeared to have maximum activity.

## Results

Earlier workers reported an essentially linear relationship between the band position and the mole fraction Hf in the Hf–Zr mixed oxides;[9] the solid line in Figure 2 represents data reported in ref 9. The preparative method in ref 9 utilized precipitation and washing procedures that are analogous to those used in the present study; however, following drying at 120 °C the solids in ref 9 were calcined at 1650 °C for 6–8 h. In this study, portions of solids containing 40, 60, or 80 mol % Hf were calcined in air at 1000 °C for 6 h. After calcination at 1000 °C, the wavelength for the most intense band for each of these samples (solid points in Figure 2) agreed very closely to those of ref 9 (solid line in Figure 2). Thus, our bulk samples, after calcining at 1000 °C, give results that are essentially the same as reported by earlier workers.

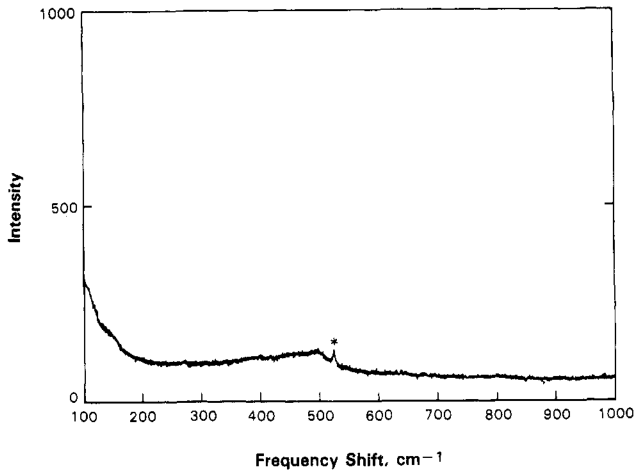

**Figure 3.** Raman spectrum for pure hafnia after calcination at 1000 °C (* indicates plasma peak).

Also included in Figure 2 are three data points representing the band position for the most intense band for zirconia that had, prior to calcination, 40, 60, or 80% surface coverage by $HfO_2$. For these three samples the band position is very close to that obtained for pure zirconia; it appears that the hafnia impregnated onto the surface diffused into the bulk during calcination at 1000 °C. Since the zirconia used for the impregnation had an area of approximately 40 $m^2/g$, even a complete monolayer of Hf is not enough, if randomly distributed throughout the bulk, to alter the most intense Raman band position for these samples from that of pure $ZrO_2$.

Difficulties were encountered in recording the Raman spectra with hafnia and mixed metal oxide samples with the higher Hf content that were not observed with pure zirconia. An intense background was superimposed upon the expected spectra which, for samples with the higher hafnium content, could mask the bands expected for the oxide sample. Furthermore, the extent of background interference depended upon both the calcination temperature and the hafnium content. Krebs and Condrate[9] did not report that the background was a problem for $HfO_2$ calcined in air at 1650 °C. We did not encounter problems with this background for samples containing up to 80 mol % $HfO_2$ that had been calcined in air at 1000 °C. However, as shown in Figure 3, the Raman spectrum for a sample of pure $HfO_2$, after calcination at 1000 °C, exhibited no distinct peaks that characterize the monoclinic phase of hafnia or zirconia (the one observed peak is a plasma line). The X-ray diffraction (XRD) pattern for this $HfO_2$ sample, after 4 h calcination at either 600 or 1000 °C, was identical with that expected for the monoclinic phase $HfO_2$. The XRD pattern for the material after calcination at 1000 °C is shown in Figure 4. The two XRD peaks confirm that the material has the monoclinic phase structure since both cubic and tetragonal phases have a single peak at a $2\theta$ position that falls between the two large peaks in Figure 4. The narrow lines confirm that the material has a large (>60 nm) crystallite size. Therefore, we have a material that has, after 1000 °C calcination, the monoclinic phase structure but does not exhibit the expected Raman spectrum.

The background is also prominent in the spectra of some of the mixed Hf–Zr oxides following calcination at 600 °C. The Raman spectrum for the bulk sample containing 40% Hf that was calcined at 600 °C (Figure 5B) is similar to one obtained for pure $ZrO_2$ that had been calcined at 600 °C (Figure 5A). However, the spectrum for the 40% Hf sample has more background, the Raman bands are less intense, and the bands appear broadened compared to the spectrum for $ZrO_2$ (Figure 5A). The background obscured the bands for both the 60% and 80% $HfO_2$ samples; note that a signal level of 11 000 Hz has been subtracted from the spectra for the 80% $HfO_2$ sample (Figure 5C,D).

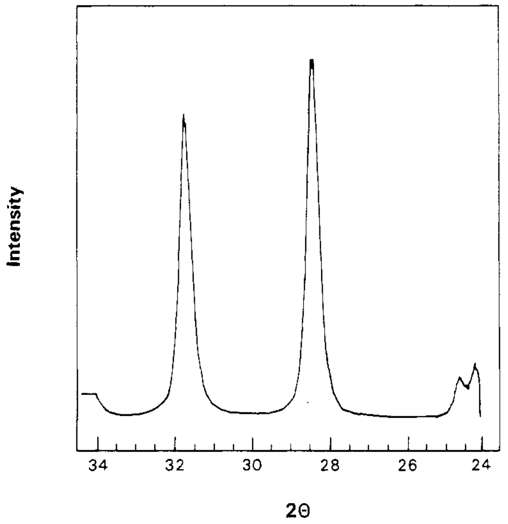

**Figure 4.** X-ray diffraction pattern for hafnia calcined at 1000 °C (same sample used to obtain Figure 3 data).

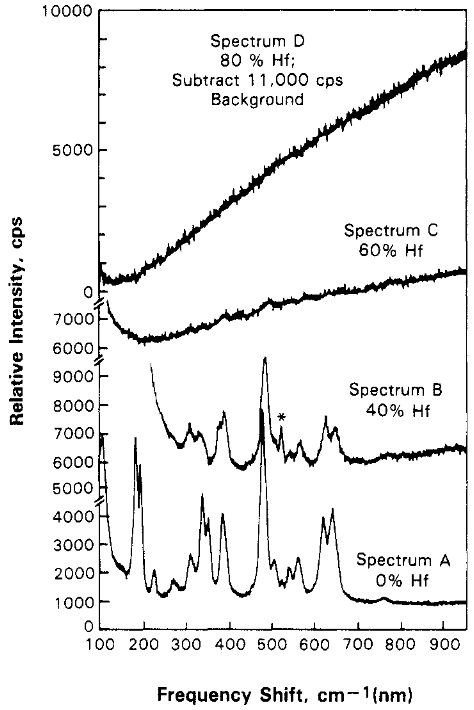

**Figure 5.** Raman spectra following sample calcination at 600 °C for (A) pure zirconia; (B) 40% hafnia coprecipitated sample; (C) 60% hafnia coprecipitated sample; and (D) 80% hafnia coprecipitated sample (note background subtraction).

The impact of calcination temperature upon the Raman spectrum is demonstrated in Figures 5D and 6. Whereas the Raman spectrum obtained for the 80% $HfO_2$ sample after calcination at 600 °C shows only the background (Figure 5D), the Raman spectrum (Figure 6) recorded following calcination of a portion of this sample at 1000 °C is very similar to those obtained by earlier investigators.[9,11]

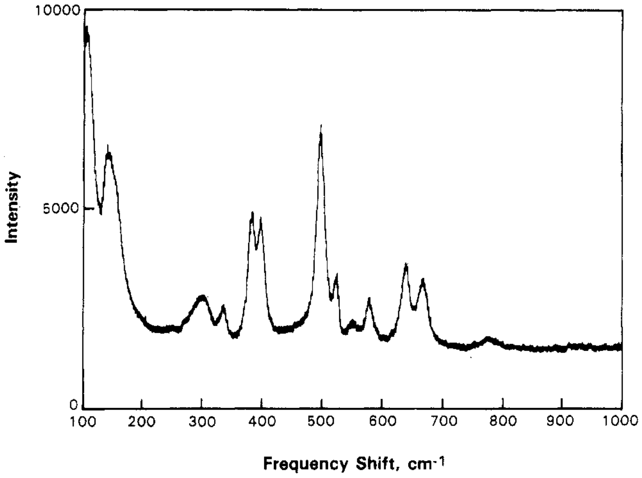

**Figure 6.** Raman spectrum of 80% Hf mixed metal oxide sample following calcination at 1000 °C.

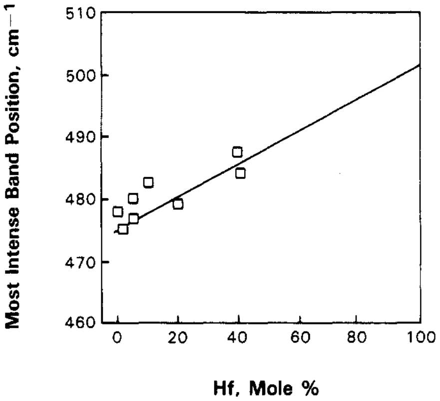

**Figure 7.** Position for the most intense Raman band for monoclinic zirconia and hafnia–zirconia mixtures after calcination at 600 °C (solid line represents data from ref 9).

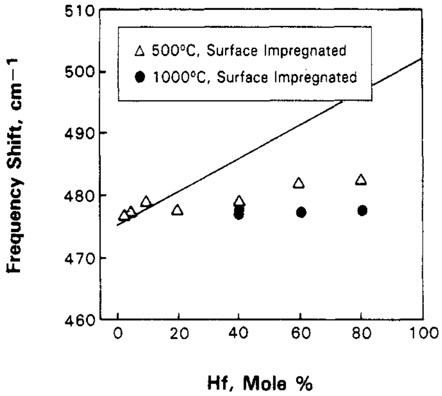

**Figure 8.** Position for the most intense Raman band for monoclinic zirconia impregnated with hafnia to produce surface loadings from 1 to 80% surface coverage following calcination at 500 °C (Δ) and 1000 °C (●) (solid line represents data from ref 9).

The intense background for 600 °C calcined materials prevented us from obtaining a band position for oxide samples with a bulk composition of 60% Hf or higher. However, the position of the most intense band for samples containing 40% or less of Hf, following calcination at 600 °C, agrees reasonably well with those reported in ref 9 for materials calcined at 1650 °C (Figure 7).

The Raman spectra for samples of $ZrO_2$ with various $HfO_2$ surface coverage have some similarities to those of the corresponding bulk sample. The background is present for samples with the higher Hf surface coverage. However, the background is not as great, for similar Hf compositions, for the surface impregnated sample as it is for the corresponding bulk sample provided both samples were calcined at 600 °C. Consequently,

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(11) (a) Kermidas, V. G.; White, W. B. *J. Am. Ceram. Soc.* **1974**, *57*, 22. (b) Anastassakis, E.; Papanicolaou, B.; Asher, I. M. *J. Phys. Chem. Solids* **1975**, *36*, 667. (c) Keramidas, V. G.; White, W. B. *J. Am. Ceram. Soc.*, **1974**, *57*, 22. (d) Phillippi, C. M.; Mazdiyasni, K. S. *J. Am. Ceram. Soc.* **1971**, *54*, 254. (e) Ishigame, M.; Sakurai, T. *J. Am. Ceram. Soc.* **1977**, *60*, 367. (f) Perry, C. H.; Liu, D.-W. *J. Am. Ceram. Soc.* **1985**, *68*, C-184. (g) Voron'ko, Yu. K.; Ignat'ev, B. V.; Lomonova, E. E.; Osiko, V. V.; Sobol, A. A. *Sov. Phys. Solid State* **1980**, *22*, 603 (pp 1034–1038 in Russian original). (h) Ignat'ev, B. V.; Kalabukhova, V. G.; Osiko, V. V.; Sobol, A. A. *Sov. Phys. Solid State* **1980**, *22*, 890 (pp 1524–1526 in Russian original). (i) Aleksandrov, V. I.; Voron'ko, Yu. K.; Ignat'ev, B. V.; Lomonova, E. E.; Osiko, V. V.; Sobol, A. A. *Sov. Phys. Solid State* **1978**, *20*, 305 (pp 528–534 in Russian original).

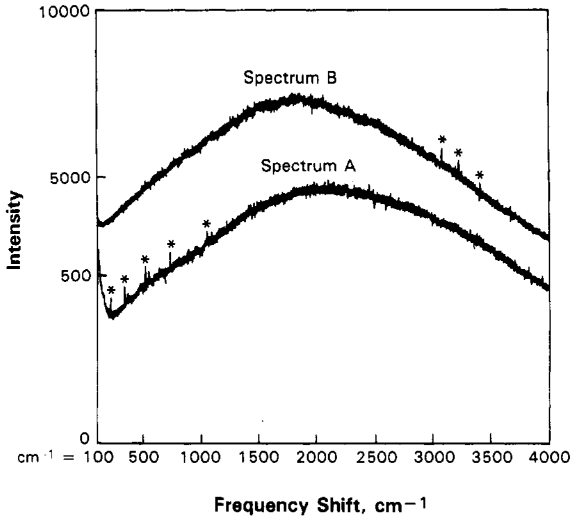

**Figure 9.** Wide frequency range Raman spectra using for (A) the 488.0-nm and (B) the 514.5-nm line of the argon ion laser (* indicates plasma lines; spectra in figure are for the 60% Hf sample).

the band position of the most intense peak can be measured for a higher Hf concentration for a surface impregnation sample than for the corresponding bulk samples. However, the position of the most intense band does not shift with Hf concentration for the surface impregnated samples to nearly the extent that it does for the corresponding bulk sample (Figures 7 and 8). In addition, heating the hafnia surface impregnated zirconia samples to 1000 °C produces materials that have Raman spectra that are essentially the same as pure $ZrO_2$ (Figure 8). Apparently the Hf becomes mobile between 600 and 1000 °C and diffuses into the bulk where, even for zirconia with 100% Hf surface coverage, there is insufficient Hf to produce a bulk composition that has sufficient Hf to alter the Raman spectrum from that of pure zirconia.

It could be anticipated that the amount of background would significantly depend upon the wavelength of the laser irradiation. Both the 488.0- and 514.5-nm lines of the argon ion laser were used and Raman spectra were recorded over a much wider frequency range for both the 60% and 80% bulk Hf oxides (Figure 9). The broad background peak is present when either of these frequencies is used; however, it is necessary to obtain Raman spectra using a wider range of excitation frequencies to learn more about the nature of the background.

## Discussion

The thermodynamic and chemical properties of $HfO_2$ and $ZrO_2$ are so similar that deviation, if any, from an ideal solid solution should be insignificant. The free energy of the monoclinic and tetragonal phases of pure zirconia differ by about 5.9 kJ/mol at a transition temperature of about 1150 °C.[12] The heats of formation of the two oxides are similar[13] so that this should not be a strong driving force for surface enrichment by one metal. However, the abrupt change in catalytic activity (Figure 1) is not anticipated if there is a uniform change in surface composition that parallels the bulk composition. For the surface impregnated zirconia, a mixture of 2-butanol and 2-octanol (90 mol %) was used as reactant; similar results were obtained for the olefins produced in the conversion of each alcohol (Figures 1 and 10). A surface enrichment to provide essentially a hafnia surface could explain the results in Figures 1 and 10 for compositions from pure hafnia to about 80–90% zirconium. However, it would also be necessary for the hafnia enrichment to abruptly end where the break in olefin selectivity occurs, and beyond this composition the surface must be enriched in Zr. In view of the similar catalytic activities of pure hafnia and zirconia, and of the mixed metal oxides, the abrupt selectivity change cannot be due to an abrupt change in catalytic activity. Differences in surface area likewise cannot account for the observed selectivity change.[8] Thus, it becomes important to verify that an abrupt change in surface composition does not parallel the selectivity change and that the bulk composition is uniform throughout the sample.

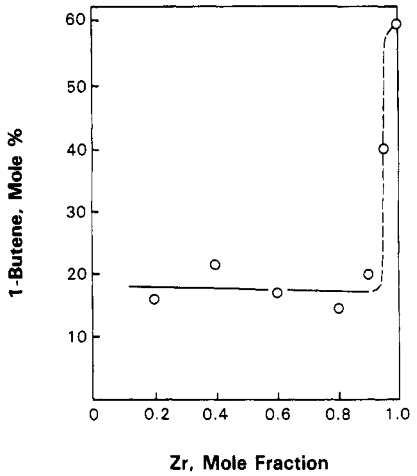

**Figure 10.** Olefin selectivity from the dehydration of a 2-butanol (10 mol %) and 2-octanol mixture with hafnia impregnated zirconia at 250 °C.

For zirconia and hafnia, the crystal phase may be identified by the distinct Raman spectra, differing both in the number of peaks and in the frequency of the bands present for the crystal phase present. For the mixed Hf–Zr oxides, the frequency of several of the more intense bands is linearly related to the bulk composition.[9,11] We have verified that, except for pure hafnia, the Raman spectra and the band positions are those expected for essentially ideal solid solutions.

Hafnia, after calcination at 1650 °C, is reported to have a spectrum that is similar to that obtained for monoclinic zirconia.[9] We find, however, that the Raman spectrum for hafnia calcined at only 1000 °C is a broad background without distinct peaks. It therefore appears that the source of background is associated with surface Hf atoms. Furthermore, it appears that the calcination temperature required to eliminate the background increases as the Hf surface fraction increases.

It does not appear that the background intensity is simply related to the number of surface Hf atoms. If one considers the materials calcined at 600 °C, the surface areas for these materials are[8] 0.4 Hf, 36 $m^2/g$; 0.6 Hf, 24 $m^2/g$; and 0.8 Hf, 20 $m^2/g$. If we assume that the surface composition is the same as the bulk, the 0.4 Hf bulk sample has the same number of Hf surface atoms as the 0.6 Hf bulk sample and 0.9 as many surface atoms as the 0.8 Hf bulk sample. However, the background dominates the Raman spectra for both the 0.6 and 0.8 Hf samples while distinct peaks are present for the 0.4 Hf bulk sample. We can also compare the ratio of surface Hf atoms in the pure $HfO_2$ calcined at 1000 °C with a surface area of 1 $m^2/g$ or less to the 0.4 bulk Hf sample assuming equal bulk and surface Hf fraction; on this basis the 0.4 bulk Hf sample has about 14 times as many surface Hf atoms as the pure $HfO_2$ sample. Since the pure $HfO_2$ spectrum does not contain distinct peaks and the 0.4 bulk sample does, it appears that the background could only be related to the number of surface Hf atoms even if the surface fraction was much less than the bulk fraction for the mixed oxides. For the preceding specific example, the 0.4 bulk Hf sample could only have the same number of Hf atoms as pure $HfO_2$ calcined at 1000 °C if the surface fraction was less than 0.03, a conclusion inconsistent with the surface analysis data presented in ref 8. Consequently, it appears that the background is caused by a hafnium structure, or structures, which probably require two, or more, neighboring Hf atoms.

The background appears to provide an additional means to identify surface Hf atoms and to augment the band shift as a means of recognizing surface composition changes. However, at this point we do not have an explanation for this. Others have

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reported that background prevents, or makes difficult, the acquisition of quality Raman data. For example, Stencel et al.[14] recently reported that difficulties in obtaining spectra were encountered due to an intense fluorescence background for Mo–$SiO_2$ catalysts with loadings of Mo below 5%. In this case, however, the chemical structure responsible for fluorescence was not identified.

Transition-metal ion (particularly $Fe^{3+}$) impurities,[15] color centers and crystal defects,[15,16] and surface and bulk excitons[17] have been discussed as possible origins of the scattering background. Careri et al.[18] related the scattering background to the presence of water molecules tightly hydrogen bonded close to Lewis acid sites and showed the intensity of the scattering background was strongly dependent on the nature of the oxide. Jeziorowski and Knozinger[19] showed that surface hydroxide ions were responsible for the so-called "fluorescence" background for MgO and $Al_2O_3$. These latter authors obtain a clear correlation between background intensity and hydroxyl group density of the MgO surface. For alumina, the latter authors detected two distinct hydroxyl groups which they tentatively attributed to terminal –OH groups coordinated to a tetrahedral or an octahedral cation, respectively. In light of the observations of Jeziorowski and Knozinger, it appears likely that the intense background for the higher Hf containing materials is due to hydroxyls or water. If this is the case then either (1) the Hf would have to retain water or hydroxyls much more strongly than Zr or (2) the hydroxyls associated with Hf, but not those with Zr, are responsible for the background. However, either of these two cases would be surprising.

The Raman data and the surface characterization data in ref 8 are consistent with a surface Hf composition that is very close to that of the bulk. From the similarity of the surface analysis and Raman data for the surface impregnated and bulk samples, it is concluded that the Hf added to the surface by impregnation of the calcined zirconia remains on the surface even following calcination at 600 °C. Upon heating to 1000 °C, the surface Hf becomes mobile and diffuses into the bulk.

The surface characterization data therefore indicate that the surface fraction of Hf is essentially equal to the bulk fraction for coprecipitated catalysts. Furthermore, the impregnated sample retained the Hf on the surface to provide the composition prepared by impregnation. In this respect it appears that the hafnium oxide–zirconium oxide system provides an excellent catalyst system for evaluating the importance of surface or bulk factors in determining catalytic properties. However, the selectivity for alcohol dehydration, while interesting in itself, appears to be too complex to be used for this purpose.

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**Registry No.** $HfO_2$, 12055-23-1; $ZrO_2$, 1314-23-4.

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# Second Harmonic Generation Studies of Hydrogen Evolution from Polycrystalline Silver Electrodes in Acetonitrile

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The optical second harmonic generation from polycrystalline silver electrodes decreases in a reversible manner during the evolution of molecular hydrogen in acetonitrile solutions containing a variety of acids. The observed changes are ascribed to the modification of the nonlinear response of the electrons at the metal surface by the adsorption of a monatomic hydrogen species. The relative surface coverage of adsorbed hydrogen as a function of potential and of acid strength can be calculated from the optical data; a comparison of the calculated surface coverages with those predicted from various models reveals the reaction mechanism for the formation of molecular hydrogen. The hydrogen evolution reaction on silver electrodes in acetonitrile proceeds via a two-step process: an initial ion-discharge reaction which creates an adsorbed monatomic hydrogen species on the surface, followed by a biatomic surface combination reaction.

## Introduction

The nonlinear process of optical second harmonic generation (SHG) is inherently sensitive to the interface of two centrosymmetric media. This sensitivity arises from the relaxation of the bulk symmetry at the interface (SHG is an electric dipole forbidden process in centrosymmetric media)[1] and has led to a significant increase in the interest and use of SHG as a spectroscopic probe of surfaces.[2] In particular, SHG has been used extensively as an in situ measurement on polycrystalline and single-crystal silver electrodes.[3-11] A number of SHG studies have measured

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