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(19) This observation is borne out by the hydrogen affinities of olefin ions which can be calculated from the results obtained or cited here. For instance, based on the heats of formation of the alkyl ions derived in the concluding sections of this paper and cited in the third column of Table VI, the hydrogen affinities of olefin ions with internal double bonds are (kcal/mol) 2-$C_4H_8^+$, 83.4; c-$C_5H_8^+$, 84.3; c-$C_5H_7CH_3^+$, 83.9. For olefin ions with terminal double bonds one obtains $CH_3CHCH_2^+$, 96.6; 1-$C_4H_8^+$, 94.4; *i*-$C_4H_8^+$, 98.0.
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A Vibrational Study of Zirconium Tetraborohydride Supported on Aluminum Oxide. 1. Interactions with Deuterium, Deuterium Oxide, and Water Vapor

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Abstract: Supported complexes, formed by grafting known homogeneous catalytic compounds onto support materials, are currently of significant interest and have great potential value in industrial applications. Progress in this field, however, has been hampered by a lack of information about the structure of the supported complexes. In the current study, inelastic electron tunneling spectroscopy (IETS) has been used to probe the vibrational structure of $Zr(BH_4)_4$ supported on Al_2O_3 as a function of temperature between 300 and 475 K. A number of surface species have been identified. Interactions of the supported zirconium complex with H_2O, D_2O, and D_2 have been observed also over the same temperature range. Vibrational transitions throughout the entire spectral range from 240 to 4000 cm^{-1} are clearly observed, and peak assignments are presented based on vibrational results available for a number of related compounds and systems. This study demonstrates the utility of IETS and at the same time provides significant new insight on a system of considerable interest and importance.

Introduction

Since 1970, there has been increasing interest in attempts to form new types of catalysts combining the desirable features of both homogeneous and heterogeneous catalytic systems.[1] Traditionally, heterogeneous systems have provided for easy separation of catalyst from products, good catalyst stability, and high activity. Homogeneous catalysts, while being often expensive, fragile compounds easily lost due to separation problems, can typically provide greater selectivity, and can be tailored and adapted to fit a specific process in a more logical and easy fashion than their heterogeneous counterparts. Efforts to combine the advantages from both areas into a new class of catalysts have centered on attempts to graft or anchor homogeneous catalytic compounds onto high surface area supports

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(see, for example, ref 1 and references cited therein). These supported complexes have formed a new class, or "third generation", of catalysts which span both the homogeneous and heterogeneous areas, and already are of considerable industrial importance. An additional important feature of many of the supported complexes observed thus far has been a significant increase in catalytic activity relative to the homogeneous analogues.[1,2] Increases in activity of up to four orders of magnitude resulting from grafting a complex onto a support have been reported.[3] Interactions between homogeneous catalytic compounds and supports evidently ensure and/or increase the number of complexes existing in a form required to produce catalytically active sites or centers.

There are, however, difficulties and inconveniences associated with grafting complexes onto supports, the most serious apparently being an accompanying loss of knowledge concerning the structure of the complex. To date, there is very little detailed structural information available for any supported complexes. (No definite proof of any structure for such a complex has yet been reported.) In general, the number and nature of any ligands which remain associated with a complex on the surface are not known. Also, the support itself, in addition to insolubilizing and dispersing the catalytic compounds, might provide a cooperative effect and function as a cocatalyst or activating agent. Little is known or understood about such possible effects. This lack of understanding concerning the nature and structure of supported complexes is hindering progress in the field. One working group, formed to examine the status of catalysis by supported complexes, has reported that the deficiency of detailed structural information is holding up advances in this area and that "significant progress is impossible unless new techniques are exploited".[4]

Recently, we have reported preliminary results of the vibrational structure of $Zr(BH_4)_4$ supported on aluminum oxide at 300 K.[5] Vibrational data were obtained by utilizing inelastic electron tunneling spectroscopy (IETS), a relatively new technique which has been shown to be an effective means of probing the vibrational structure of molecules adsorbed on insulating surfaces. $Zr(BH_4)_4$ is one of several metal tetraborohydrides which have proved effective in catalyzing polymerization reactions of olefins.[6,7] While the rate of polymerization in solution is rather low, greatly enhanced activity has been obtained by interacting $Zr(BH_4)_4$ with various supports. Grafting $Zr(BH_4)_4$ onto Al_2O_3 has produced more active catalysts than have been obtained using other supports.[3] Although $Zr(BH_4)_4/Al_2O_3$ is an effective olefin polymerization catalyst, the exact nature and behavior of even the unsupported complex, particularly the nature of the metal–BH_4 interaction, during reaction are not known.

This study represents part of a continuing effort to understand the behavior of Al_2O_3-supported $Zr(BH_4)_4$ catalytic systems. In the following sections, we will outline for experimental procedures, and report and discuss vibrational spectra obtained with IETS for $Zr(BH_4)_4$ on Al_2O_3 as a function of temperature, as well as for its reactions with H_2O, D_2O, and D_2. The final section is a summary of the major findings of this study. The following paper deals with the interactions of $Zr(BH_4)_4/Al_2O_3$ with ethylene, propylene, and acetylene.

Experimental Section

IETS involves monitoring the current produced by electrons tunneling through a thin insulating barrier between two metal electrodes when a bias voltage is placed across the barrier. The conductance of such a metal-insulator-metal tunnel junction exhibits increases in magnitude at values of the bias voltage which correspond to vibrational excitation energies of molecules in the barrier region. These conductance increases arise from additional channels becoming available for tunneling electrons which traverse the insulating barrier inelastically (i.e., with a net energy loss) by exciting vibrational modes of molecules in or near the barrier. A derivative spectrum presenting d^2V/dI^2 (proportional to the second derivative of the current, d^2I/dV^2) as a function of the applied voltage, V, yields a series of peaks the positions of which correspond to vibrational excitation energies for molecules in the barrier region. Spectra obtained in this manner have been shown to be analogous to those obtained by optical absorption spectroscopies such as IR or Raman (both IR- and Raman-active modes being observed in the tunneling spectra).[8]

In our application of the IETS technique, samples are prepared in an oil diffusion pumped bell jar with a base pressure of 10^{-7} Torr. A thin aluminum strip is evaporated onto a clean glass substrate; then the top few atomic layers of the strip are oxidized in a plasma discharge of pure O_2. This thin (20–30 Å) layer of Al_2O_3 forms the insulating barrier required for IET experiments, and additionally serves as the aluminum oxide substrate used for supporting the $Zr(BH_4)_4$. Loading of the zirconium complex onto the support was accomplished by exposing the Al_2O_3 films to 5×10^{-2} Torr of $Zr(BH_4)_4$ for 15 min (a surface area of approximately 1 mm^2 being probed during measurement). This exposure was sufficient to produce a saturation coverage of adsorbate on the surface as judged by the lack of any observed changes in the vibrational spectra for higher exposures. Unused $Zr(BH_4)_4$ vapor was collected in a liquid N_2 cooled trap and transferred under vacuum to a collection cylinder, since exposure to air can result in fire and/or explosion. Samples were then heated to various temperatures between 300 and 475 K for up to 30 min under either vacuum, 5 Torr of D_2, or 1 Torr of N_2, H_2O, or D_2O. (Samples which were exposed to $Zr(BH_4)_4$ and then heated showed no differences in this temperature range from samples where the substrate was heated during exposure to the complex.) Sample heating was accomplished via a resistive heating technique developed by Bowser and Weinberg.[9] Lastly, a Pb cross strip was evaporated on top of the sample, the Pb and underlying Al layers serving as the two metal electrodes required for the tunneling measurements. Previous IETS studies have shown that interactions between adsorbed species and the Pb overlayer are generally negligible.[10] None of the spectral features observed in the current study is an indication of any such interactions. Measurements were carried out over the entire spectral range from 240 to 4000 cm^{-1} via standard techniques. Measurements for several samples at each set of conditions were made to ensure reproducibility. Spectral features can typically be resolved to within ± 4 cm^{-1}. Further details of both experimental and theoretical aspects of IETS are available elsewhere.[10]

Results

The spectrum for $Zr(BH_4)_4$ on aluminum oxide at 300 K, reported earlier in a preliminary communication,[5] is presented in Figure 1. Peak positions are also identified in this figure. The spectrum for this system is presented again for comparative purposes in Figure 2 along with spectra for $Zr(BH_4)_4/Al_2O_3$ exposed to D_2 or D_2O at both 300 and 475 K, and to vacuum and H_2O at 475 K. No discernible differences were evident between samples heated under vacuum and those heated in N_2. It should be noted that the 1000–1500- and 1500–4000-cm^{-1} regions of the spectra in Figure 2 have been enhanced by factors of 3 and 1.5, respectively, relative to the region below 1000 cm^{-1}. Peak positions for each of the spectra shown are listed in Table I. Spectra measured for samples at intermediate temperatures are not shown since they contribute little additional information. Temperature had little, if any, noticeable effect on samples exposed to either H_2O or D_2O.

At 300 K (see especially Figure 1), the supported complex showed low-energy bands at 264 and 299 cm^{-1}, a shoulder near 323 cm^{-1}, and unresolved low-intensity structure between approximately 480 and 580 cm^{-1}. A stronger, broad peak appears near 693 cm^{-1}. The most intense spectral feature consists of a rather sharp peak at 910 cm^{-1} with a strong high-energy shoulder at 945 cm^{-1}. Between 1000 and 1500 cm^{-1} there are two relatively strong, rather sharp peaks at 1106 and 1260 cm^{-1} (the former with an unresolved shoulder near 1130 cm^{-1}), two broad, rounded peaks of lower intensity at 1378 and 1457 cm^{-1}, and weak features near 1030, 1173, and 1220 cm^{-1}. An extremely broad feature of varying intensity appears in all the spectra near 1870 cm^{-1}. Structure in the 2100–2300-cm^{-1} region can be resolved into at least four

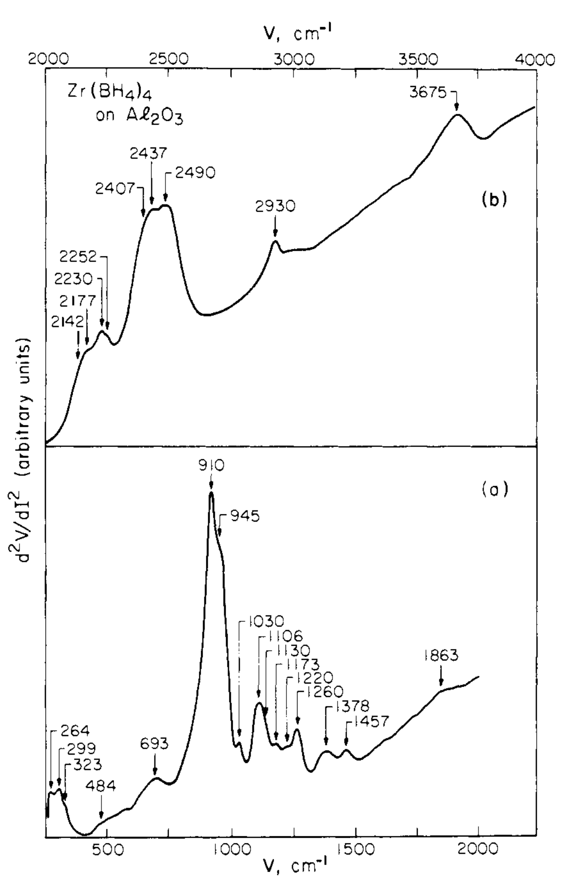


Figure 1. IET spectrum for $Zr(BH_4)_4$ absorbed on Al_2O_3 at 300 K over the spectral ranges (a) 240-2000 and (b) 2000-4000 cm^{-1}. Substrate features which have been documented previously include an Al phonon in the underlying Al film (299 cm^{-1}), the Al-O stretch of bulk Al_2O_3 (945 cm^{-1}) and its harmonic overtone (1863 cm^{-1}), the C-H stretch of contaminant hydrocarbons (2930 cm^{-1}), and the O-H stretch of surface hydroxyl groups (3675 cm^{-1}).

features (at 2142, 2177, 2230, and 2252 cm^{-1}), while at least three rather intense features can be discerned between 2400 and 2500 cm^{-1} (approximately at 2407, 2437, and 2490 cm^{-1}). Although more individual peaks may exist in these areas, they cannot be resolved adequately owing to overlap with other closely spaced features. Broad features also appear near 2930 and 3675 cm^{-1}.

Heating the $Zr(BH_4)_4/Al_2O_3$ system to 475 K produced a slight decrease in intensity for features in the 1000-1300-cm^{-1} region and for the unresolved structure between 480 and 580 cm^{-1}, with a concomitant enhancement of the 1378- and, especially, 1457-cm^{-1} peaks. This apparent enhancement might be due only to the changing shape of the background resulting from intensity decreases below 1300 cm^{-1}. Only a slightly raised background remains between 2140 and 2160 cm^{-1}. Features near 2407, 2437, and, particularly, 2490 cm^{-1} have decreased in intensity and appear only as a single, very broad, rounded feature, the highest point being near 2455 cm^{-1}.

Similar changes occur also when the supported complex is exposed to D_2 at 300 K, although both the increases and the decreases in intensity are more pronounced. Additionally, the 264-cm^{-1} peak is significantly reduced in intensity as is the peak at 910 cm^{-1}. Heating in D_2 to 475 K further reduces the intensity of the 910-cm^{-1} peak to a point where it is approximately equal in intensity to the 945-cm^{-1} feature. No structure above the normal background remains in the 480-580- and 2140-2260-cm^{-1} regions. Intensity in the 2400-2500-cm^{-1} region is further reduced as are the intensities of peaks between 1000 and 1300 cm^{-1}, except for the 1260-cm^{-1} peak, which has apparently experienced no additional intensity decrease.

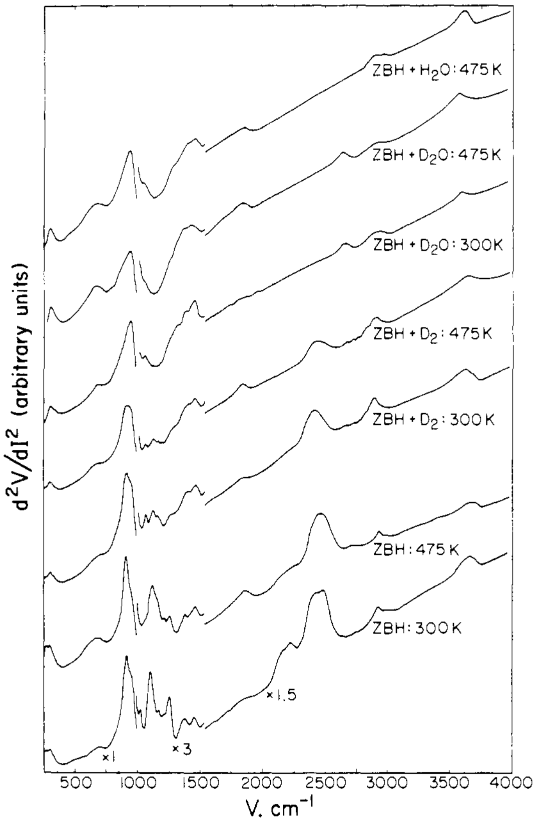


Figure 2. IET spectra over the range of 240-4000 cm^{-1} for $Zr(BH_4)_4$, designated "ZBH", adsorbed on Al_2O_3 at 300 and 475 K, and for the supported complex after exposure to D_2, D_2O, and H_2O at the same temperatures.

Samples exposed to either H_2O or D_2O are characterized by a complete loss of structure in the 480-580-, 1100-1250-, and 2100-2500-cm^{-1} regions. The 1260-cm^{-1} peak is reduced in intensity but is still present. The 910-cm^{-1} peak has been reduced to only a shoulder on the 945-cm^{-1} feature. The 264-cm^{-1} peak is greatly reduced. Enhancement of the 1450- and, to a lesser extent, the 1380-cm^{-1} features might result only from the changing nature of the background (as mentioned earlier) rather than from an actual net increase in intensity. A new, broad, low-intensity feature might be present near 1300 cm^{-1} in both H_2O and D_2O samples. A broad peak near 2670 cm^{-1} appears in samples exposed to D_2O.

Discussion

A. Adsorbate Features. As a first step in interpreting the spectra shown in Figures 1 and 2, it is possible to identify those features not associated with the supported zirconium complex itself via comparisons with published spectra of "clean" aluminum oxide surfaces. On this basis, the following assignments can be made: the peak at 299 cm^{-1} is due to a phonon in the underlying Al film; the strong shoulder at 945 cm^{-1} is a bulk Al-O stretch, the weak feature near 1870 cm^{-1} being the harmonic overtone of this peak; features near 2930 and 3675 cm^{-1} can be assigned to the C-H stretch of contaminant hydrocarbons and the O-H stretch of surface hydroxyl groups, respectively.[11] Surface OH groups have been observed in all previous tunneling experiments on aluminum oxides, resulting primarily from H_2O impurities in the background.[10] Additionally, various modes of hydrocarbon contaminants may also be contributing some intensity to features at 1030, 1378, and 1475 cm^{-1}, although other species also have characteristic transitions in these areas.

B. Structure of Zirconium Borohydrides. As a pure component, $Zr(BH)_4$ has been studied extensively by a variety of

Table I. Peak Positions (cm^{-1}) for $Zr(BH_4)_4$ Supported on Al_2O_3

under vacuum		exposed to D_2		exposed to D_2O or H_2O		
300 K	475 K	300 K	475 K	300 K	475 K	assignments
264	264	264	264			BH_4-Zr-BH_4 bend or Zr-BH_4 torsion
299	299	299	299	299	299	Al phonon
323	323	323	323	323	323	metal-oxide or Zr-BH_4 torsion
480-580	480-580					Zr-BH_4 stretch or Zr-O modes
693	685	705	693	693	695	Zr-O stretch
910	910	910	910	possible sh near 910		Zr-O stretch
945	945	945	945	942	942	bulk Al-O stretch
1030		1056	1056	1048	1048	CH bend (contamination)
1106	1106	1114	1114			BH deformation
1130	1121					
1173	1165	1165	1170			
1220	1214					
1260	1252	1257	1260	1258	1258	BH deformation and B-O stretch
			(possible weak feature near 1300)			
1378	1378	1378	1385	1374	1380	B-O modes
1457	1457	1457	1457	1450	1450	
1870	1873	1868	1870	1870	1870	harmonic of 945 cm^{-1}
2142						bridging B-H stretch
2177	2137-2258 (weak-broad)					
2230						
2252						
2407						
2437	2455 (broad)	2455 (broad)	2455 (broad)			terminal B-H stretch
2490						
				2670	2670 (D_2O only)	O-D stretch
2930	2930	2930	2930	2930	2930	CH stretch (contamination)
				3615	3615 (D_2O)	O-H stretch for D_2O exposure only
3675	3675	3669	3669	3640	3640 (H_2O)	O-H stretch for all other samples

techniques, including X-ray[12] and electron[13] diffraction, and NMR,[14,15] IR,[15-19] Raman,[16-20] and photoelectron[21] spectroscopies. An analysis of these results indicates that the boron atoms are arranged tetrahedrally around the central zirconium atom, each boron being bonded to the zirconium through three bridging hydrogen atoms (designated H_b), leaving a single terminal hydrogen (H_t). Among zirconium complexes, this type of tridentate bond appears to be restricted only to species with four BH_4 ligands. In related complexes such as $(C_5H_5)_2Zr(BH_4)_2$ and $(C_5H_5)_2Zr(H)BH_4$, the bonding between the zirconium and boron atoms is interpreted as being bidentate, i.e., occurring through only two bridging hydrogens.[6,7,16] Bidentate hydrogen bridges are also formed in complex anions such as $Li^+[Zr(BH_4)_5^-]$.[7] No evidence for monodentate bonding in zirconium complexes has yet been presented.

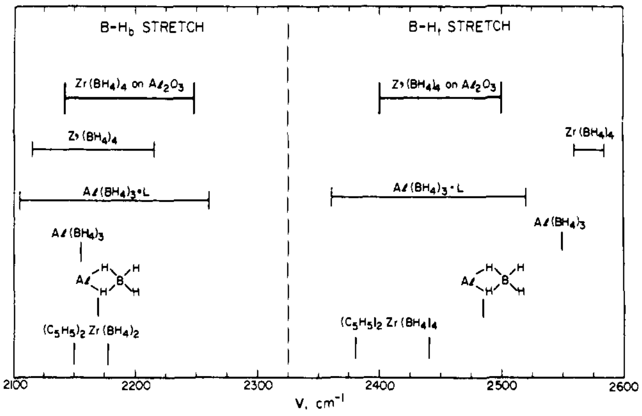
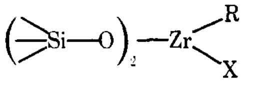
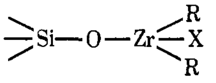


Figure 3. Comparison of both terminal (H_t) and bridging (H_b) B-H stretching frequencies for $Zr(BH_4)_4$ supported on Al_2O_3 with the corresponding vibrations for $Zr(BH_4)_4$ (ref 17); $Al(BH_4)_3$·L, where L is a coordination ligand (ref 6); $Al(BH_4)_3$ (ref 6); AlH_2BH_2, resulting from diborane absorption on Al_2O_3 (ref 27); $(C_5H_5)_2Zr(BH_4)_4$ (ref 28).

C. Adsorbed Zirconium Complexes. During $Zr(BH_4)_4$ adsorption, one or more of the BH_4 ligands are displaced in order to accommodate zirconium-surface bonds.[1] For supported complexes the surface becomes a virtual ligand, and can be expected to contribute both electronic and steric effects exerting an influence on the rest of the complex. Thus, we would not necessarily expect bonds between zirconium and the remaining BH_4 ligands to retain their unperturbed tridentate form; in fact, a bidentate structure would appear to be more probable. The nature of this bonding can be determined by examining the B-H stretching region of the spectrum, particularly vibrations involving the terminal hydrogens (H_t). For a tridentate bond, there is a single H_t atom, which has been shown to result in one peak between 2560 and 2580 cm^{-1}.[1,15,17,19,20] The two H_t atoms in bidentate bonds produce two peaks, both a symmetric and an asymmetric stretch, which appear at lower energies.[6,7,16] Figure 1 shows that at least three distinct features appear in the B-H_t stretching region, at 2407, 2437, and 2490 cm^{-1}. This observed energy range is compared in Figure 3 with observed transitions for the tridentate $Zr(BH_4)_4$, as well as for a number of complexes with known bidentate structure. The observed transition energies indicate a bidentate structure. At the same time, the observation of more than two B-H_t stretching modes, as well as more than two modes for B-H_b stretching (there are at least four at 2142, 2177, 2230, and 2252 cm^{-1}), suggests the presence of more than one type of complex on the surface. The most likely mode of adsorption of $Zr(BH_4)_4$ is by interacting with surface hydroxyl groups. Since the molecular nature of hydroxyl groups on the surface is not uniform, we might expect some nonuniformity among adsorbed complexes.[3] If we assume that the surface complexes have the same compositions (i.e., the same number and type of ligands, as well as identical bonding to the surface), however, then the nonuniformity of adsorption sites would generally result in a broadening of features in the vibrational spectrum rather than in the creation of additional features. It is probable, therefore, that the surface complexes do not have identical compositions.

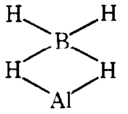
Differences in composition can occur due to the possibility of zirconium atoms becoming either singly or multiply coordinated to surface oxygen atoms. On silica, absorption of zirconium complexes with hydrocarbon and halogen ligands has been shown to produce both of the following surface species:[2,3]



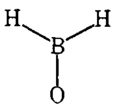


Similar results have been obtained on aluminum oxides.[2] It has been reported also that the oxidation state of zirconium can change upon adsorption to yield species containing Zr(III) and, perhaps, even Zr(II) in addition to the more prevalent Zr(IV).[3,22] (The amount of Zr in the +3 oxidation state has been estimated to be several percent of the total Zr; see ref 3 and references cited therein.) Titration with H_2 of organozirconium compounds adsorbed on silica indicates that each zirconium atom on the average retains only 1.8 of its original four ligands.[3] The presence of surface complexes with zirconium atoms both singly and multiply coordinated to surface oxygens, as well as both Zr(III) and Zr(IV) complexes, would undoubtedly result in multiple types of BH_4 ligands, corresponding to the multiple bonds observed for both terminal and bridging boron-hydrogen stretching vibrations. These differences in zirconium-oxygen coordinates should be revealed in the vibrational spectra. Multiply coordinated species might be expected to have vibrational transitions similar to those in bulk zirconium oxides or in thin zirconium oxide films. Such transitions would produce a peak near 700 cm^{-1}, and possibly weaker features near 350 and 500-570 cm^{-1}.[23] Alternately, in complexes where the zirconium-oxygen bonds are *not* bulk-like, i.e., where there is only one Zr-O bond or where one of the Zr-O bonds possesses slightly more double-bond character than any others in the same complex, vibrational frequencies would appear between 800 and 1000 cm^{-1}.[24,25] (This same frequency range has been shown to apply also to similar types of bonds for Ti, Si, Mo, V, and Cr oxide species.[25,26]) Referring again to Figure 1, peaks at 693 and 910 cm^{-1} can be assigned to these two types of zirconium-oxygen coordinations. (These peak positions also do not coincide with modes for any other proposed surface species.)

D. Other Surface Borohydride Species. Although additional peaks in the B-H stretching region can be accounted for by surface complexes with different types of Zr-O coordination (and perhaps even different Zr oxidation states), there are other possible surface species which require consideration. During adsorption of $Zr(BH_4)_4$, displaced ligands might remain on the surface, becoming associated with either Al or O atoms. ($Al(BH_4)_3$ is well known and quite stable when not exposed to air, and also has bidentate hydrogen bridging.[6]) Studies of diborane (B_2H_6) adsorption on Al_2O_3 have shown that adsorption is dissociative, resulting in formation of the following surface complexes:[27]



I



II

Similar complexes might be formed by displaced BH_4 ligands during $Zr(BH_4)_4$ adsorption. (The known slow decomposition of the zirconium complex at room temperature producing B_2H_6 presents another possible source for the above surface species.[28]) The B-H vibrations in these species would not produce unique features in the spectra (see Figure 3). Species II, however, might produce unique features due to B-O vibrations. Comparison with IR studies of B_2H_6 adsorption on Al_2O_3[27] and with vibrational studies for a number of compounds containing B-O bonds[29-33] indicates that B-O vibrations would appear in the 1200-1450-cm^{-1} range. The peaks appearing near 1378 and 1457 cm^{-1} might therefore be assigned to B-O vibrations. A B-O vibration might also be contributing to the peak at 1260 cm^{-1}, although this peak also falls in the range where B-H deformations are expected to appear (1000-1300 cm^{-1}). One report has alternately assigned the 1457-cm^{-1} peak to a BH_4 deformation mode. The remaining peak in the spectrum for adsorbed $Zr(BH_4)_4$ at 300 K appears at 264 cm^{-1}, and can be assigned to BH_4-Zr-BH_4 bending and/or Zr-BH_4 torsional modes. Features at 323 and 480-580 cm^{-1}, regions where various weak Zr-O modes could possibly be expected, might also reflect Zr-BH_4 torsional and stretching modes, respectively.[18]

E. Temperature Effects. Decomposition of zirconium borohydrides, which occurs only slowly at 300 K, proceeds rapidly above approximately 450 K evolving mainly H_2.[28] Adsorption on Al_2O_3 apparently stabilizes the complex somewhat. Examination of the spectrum for supported $Zr(BH_4)_4$ heated at 475 K (see Figure 2) indicates that, although B-H deformation and stretching modes are all reduced in intensity, some of the B-H bonds remain intact. This is in agreement with other studies which indicate enhanced thermal stability for complexes grafted onto supports.[3] Only very low intensity, unresolved structure remains in the B-H_b stretching region. The change in shape of the B-H_t stretching features indicates that surface species characterized by modes in the 2470-2500-cm^{-1} region are more sensitive to heat than are species with the lower energy B-H_t stretching vibrations.

F. Exposure to H_2O and D_2O. Zirconium and aluminum borohydrides, as well as diborane and other BH compounds, are easily hydrolyzed even at room temperature.[6] Spectra for the supported zirconium complex exposed to D_2O at both 300 and 475 K (see Figure 2) are devoid of any B-H stretching features; neither are there any new features which might be attributed to B-D modes. The absence of any possible exchange features is confirmed by comparison to the spectrum shown for H_2O exposure at 475 K, which is identical with the D_2O spectra except for a new peak near 2670 cm^{-1} in the case of D_2O. This feature can readily be assigned to the O-D stretch of surface deuteroxyl groups,[11] but since D_2O readily exchanges with hydroxyls on Al_2O_3 it is indeterminant whether the observed OD groups are attached to Zr or Al. It is important to note that the 910-cm^{-1} peak has been reduced to only a very weak shoulder on the 945-cm^{-1} feature (assigned to the bulk Al-O stretch). This is in agreement with our previous assignment of the 910-cm^{-1} feature to a Zr-O stretch for a singly coordinated (or similar type) Zr atom, the band disappearing as further zirconium-oxygen bond formation occurs during exposure to water vapor. Features at 1106, 1130, 1173, and 1220 cm^{-1}, attributed to BH_4 deformation modes, are also missing in the samples exposed to water vapor, as is the peak at 264 cm^{-1} (Zr-BH_4 bending and/or torsional modes). The peak at 1260 cm^{-1} is significantly reduced, but a weak feature still remains at this energy. This supports the assignment of this peak as a combination of B-O stretching and BH_4 deformation modes. Peaks at 1378 and 1457 cm^{-1} which were additionally ascribed to B-O modes remain also after hydrolysis, supporting their previous assignments. These peaks, especially the one at 1457 cm^{-1}, show apparent intensity increases upon exposure to water vapor, although (as discussed earlier) this might be in large part only due to the change in slope of the background in this region. There is a possible increase in intensity near 1300 cm^{-1}, although this is indefinite owing to the other overlapping features near this energy. It could arise from new types of B-O vibrations. A less likely assignment would be a Zr–H–Zr mode for incompletely oxidized zirconium atoms. These modes occur between 1240 and 1520 cm^{-1}, and have been observed to form in solutions of a number of complexes containing both Zr and H, as well as during the partial thermolysis of some zirconium borohydrides.[19,22]

G. Exposure to D_2. Exposure to D_2 fails to produce any exchange with BH groups. Although BH_4 groups are being displaced as evidenced by intensity decreases in all regions of the spectrum where B–H or Zr–BH_4 modes appear, there is not firm evidence for a new Zr–D or Zr–H stretching peak (expected near 1150[34] or 1625[3,16,19] cm^{-1}, respectively). This might be due either to the formation of Zr–H–Zr (or Zr–D–Zr) species as mentioned above or to oxidation by slight traces of O_2 or H_2O contamination. The decreasing intensity of the 910-cm^{-1} peak tends to indicate further oxidation, although the formation of Zr–H–Zr species might also be affecting this type of Zr–O bond. It is important to note that, especially for D_2 exposure at 475 K, some B–H_t bonds remain even though there are no B–H_b bonds left. This tends to confirm the presence of O–BH_2 species on the surface. That these groups are more stable with respect to both heating and reaction than other BH species on the surface is in agreement with previous reports.[27]

Conclusions

Examination of vibrational spectra obtained via IETS for Al_2O_3-supported $Zr(BH_4)_4$ reveals that during the initial adsorption a variety of surface species are formed. BH_4 ligands remaining attached to zirconium atoms, as well as any which migrate onto the support and bond to surface aluminum, change from a tridentate to a bidentate bonding geometry. Additional peaks in both the B–H_b and B–H_t stretching regions as well as two types of Zr–O stretching features indicate the nonuniformity of the surface species. The presence of O–BH_2 groups is confirmed both by the appearance of B–O vibrational modes and by the existence of B–H_t stretching modes without accompanying B–H_b vibrations. Hydrolysis occurs readily, even at 300 K. Its effects on the existing Zr–O bonds are observed in the decrease of a peak ascribed to Zr atoms singly coordinated to surface oxygen. No exchange was observed between the supported complex and either D_2 or D_2O. Vibrational modes throughout the 240–4000-cm^{-1} range were clearly observed. The successful application of IETS in this study not only demonstrates the versatility of the technique, but more importantly provides useful structural information on a type of system (i.e., a supported complex) which is becoming increasingly important in industrial catalytic processes.

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