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A Vibrational Study of Zirconium Tetraborohydride Supported on Aluminum Oxide. 2. Interactions with Ethylene, Propylene, and Acetylene

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Abstract: Supported complexes, formed by grafting homogeneous catalysts onto support materials, are becoming increasingly important in industrial applications as well as in fundamental studies. Little information is available, however, about the structures of supported complexes and the nature of their interactions with reactants. Inelastic electron tunneling spectroscopy (IETS) has here been applied to obtain vibrational spectra of $Zr(BH_4)_4/Al_2O_3$, a known polymerization catalyst for olefins, exposed to ethylene, propylene, and acetylene. These gas-surface interactions have been investigated for hydrocarbon exposures up to 6×10^3 Torr s and for temperatures between 300 and 575 K. The IET spectra (observed over the entire range from 240 to 4000 cm^{-1}) provide information regarding the types of C-C and C-H bonds present in the various surface species. Polymer formation is also revealed in the vibrational spectra. The versatility of IETS is demonstrated explicitly by providing valuable new information on a unique catalytic system of significant importance.

Introduction

In the preceding paper,[1] and in an earlier communication,[2] inelastic electron tunneling spectroscopy (IETS) has been utilized to probe the vibrational structure of $Zr(BH_4)_4$ (zirconium tetraborohydride) adsorbed on aluminum oxide. The behavior of the supported zirconium complex was observed also as a function of temperature, and for exposures to D_2, D_2O, and H_2O. Metal borohydride compounds have been of considerable interest owing both to the unique types of M-H-B bonds existing in such molecules and, more importantly, owing to their ability to catalyze polymerization reactions of olefins.[3] The rate of olefin polymerization by any individual complex, however, is relatively low compared to traditional Ziegler-Natta type catalysts.[4] Over the past several years, there has been a rapidly growing interest in the field of "supported homogeneous catalysts", catalysts formed by grafting homogeneous catalytic compounds onto support materials. These supported complexes exhibit many of the desirable features of both homogeneous and heterogeneous catalysts: they combine the greater stability and ease of separation from products characteristic of heterogeneous systems with the ability of homogeneous catalysts to be tailored selectively to fit specific reactions in a more logical and easier fashion. Research in this area has received significant impetus by the observation that grafting onto a support can increase the catalytic activity of a complex by several orders of magnitude.[4] In addition, supported complexes have been noted to produce higher degrees of crystallinity than obtained in homogeneous polymerization reactions, as the presence of the surface limits access to central metal centers and thereby establishes an orientation preference. Partial control of the degree of crystallinity can be obtained by varying the surface concentration of supported complexes, as crowding metal centers together on the surface can limit access even further.[5] (This does, however, reduce activity somewhat.) Supported complexes are already being utilized in a number of important industrial processes and, as a group, offer more promise from an applied point of view than other currently known types of catalysts.[6] Progress in the area of catalysis by supported complexes, however, has unfortunately been hindered by the lack of structural information available for the surface species.[6,7] Structural characterization of supported complexes has been very poor, plagued by many problems similar to those encountered in attempting to characterize the surfaces of traditional heterogeneous systems.[8]

The current study represents part of an ongoing effort to provide new structural information concerning supported-complex catalytic systems by utilizing an experimental probe not previously exploited in this area of research. Specifically, we have applied inelastic electron tunneling spectroscopy to obtain vibrational spectra for acetylene (C_2H_2), ethylene (C_2H_4), and propylene (C_3H_6) on alumina-supported $Zr(BH_4)_4$. Aspects of our experimental procedures unique to the current study are presented in the next section, which will be followed by presentation and, then, discussion of the results. This report will be concluded by a brief summary of some of the important results and conclusions presented herein.

Experimental Section

Inelastic electron tunneling spectroscopy (IETS) has been shown to be an effective means of monitoring the vibrational structure of molecules on or near insulating surfaces.[9] In the preceding paper, we have outlined our experimental procedures for applying IETS to the study of zirconium tetraborohydride supported on aluminum oxide. (A thorough review of both the theoretical and experimental aspects of IETS is available elsewhere.[10]) In the current work, supported zirconium complexes were allowed to interact with C_2H_2, C_2H_4, or C_3H_6. The effects of exposure (i.e., the pressure-time product) and temperature were examined for each of the hydrocarbon species.

Results

Spectral measurements were performed for samples of supported $Zr(BH_4)_4$ exposed to ethylene at exposures from 15 (5×10^{-2} Torr of C_2H_4 for 300 s) to greater than 6×10^3 Torr s (5 Torr for 1200 s), and at various temperatures between 300 and 575 K. Very little adsorption, with no resolvable structure above background contamination, was noted for lower exposures. Furthermore, no C_2H_4 adsorbs on the base Al_2O_3 under these experimental conditions. This is also true for both C_3H_6 and C_2H_2. Saturation coverage was obtained at all temperatures with exposures of 3×10^3 Torr s, as judged by the lack of any further spectral changes at higher exposures. No reproducible shifts in peak positions were observed as a function of coverage. Spectra obtained for saturation coverages of C_2H_4 at 300, 400, 450, and 575 K are shown in Figure 1. Peak positions are listed in Table I. Increasing temperatures are accompanied by increases in intensity for spectral features between 2850 and 3000 cm^{-1}, at 1380 and 1455 cm^{-1}, and the appearance of a new feature near 1300 cm^{-1}. Apparent (small) shifts seen for peaks between 2850 and 3000 cm^{-1} are probably only due to the difficulty of accurately locating positions for

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Table I. Peak Positions (cm^{-1}) for C_2H_2, C_2H_4, and C_3H_6 on Alumina-Supported $Zr(BH_4)_4$

C_2H_2		C_2H_4		C_3H_6		
300 K	400 K	300 K	525 K	300 K	525 K	assignments
264	264	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 mode or Zr-BH_4 torsion
485	485	~480 to 580	~480 to 580	490 to 580	490 to 580	Zr-BH_4 stretch, Zr-O modes, and (acetylene only) polymer skeletal deformations
573	573					
690	690	693	693	693	693	Zr-O stretch
910	910	910	910	910	910	Zr-O stretch
945	945	945	945	945	945	Al-O (bulk) stretch
1030	1030	1044?	1040?	1030	1030	CH modes
1071	1071					
1106	1106	1106	1106	1102	1102	BH deformations
1130	1130	1130	1130			
1173	1173	1169		1165		
1220	1220	1218		1213		
1260	1260	1256	1244	1258	1258	BH or B-O mode
1351	1351	1302	1302	1342	1342	C-C stretch (C_2H_2 only), CH deformations, and B-O modes
1380	1380	1383	1380	1378	1378	
1452	1452	1455	1455	1449	1449	
1597	1597					C=C stretch?
1870	1870	1870	1874	1870	1876	harmonic of 945 cm^{-1}
2150	2150	2142		2134		bridging BH stretch
2181	2177	2177		2177		
2236	2233	2229		2229		
2258	2250	2256		2252		
2410	2410	2406	2440 (broad)	2410	2410	terminal BH stretch
2434	2434	2435		2427	2427	
2484	2492	2486		2473	2473	
2505				2501	2490	
2871	2871	2879	2879	2863	2867	CH stretch
		2913	2920	2903	2899	
2935	2922	2930	2938	2930	2930	
2981	2960	2960	2958	2952	2950	
3677	3677	3677	3641	3669	3625	OH stretch

several overlapping, closely spaced features. A feature at approximately 1870 cm^{-1} also grows slightly with temperature. Alternately, modes appearing near 1106, 1130, 1169, and 1218 cm^{-1} decrease as the temperature is raised, the 1169- and 1218-cm^{-1} features not being apparent at 575 K. The intensity of features between 2100 and 2300 cm^{-1} shows corresponding decreases, no structure in this spectral region being observed above 450 K. Distinct features near 2406, 2435, and 2486 cm^{-1} at 300 K also decrease with temperature, the peak at 2486 cm^{-1} more rapidly than the others. Above 450 K, separate peaks can no longer be resolved in this spectral region; remaining structure appears only as a broad, rounded feature centered near 2440 cm^{-1}. The feature at 3672 cm^{-1} at 300 K shifts approximately 30 cm^{-1} to 3641 cm^{-1} at 575 K.

Results for saturation exposures of propylene to the supported $Zr(BH_4)_4$ at 300, 400, and 575 K are illustrated in Figure 2, peak positions being recorded also in Table I. As is the case with ethylene, increases in intensity for features at 2850-3000, 1378, and 1449 cm^{-1} accompany increasing temperature. Also, analogous to ethylene adsorption, there are intensity decreases observed for features near 1100-1250, 2100-2300, and 2400-2500 cm^{-1} with increasing temperature; however, loss of intensity in these regions is perhaps not so great as with ethylene. Of particular interest is the observation of a peak at 2501 cm^{-1}, which is more intense than others in the 2400-2500-cm^{-1} region. (If a similar feature is present in the ethylene spectra, it is only a shoulder and not such a prominent peak as in the case of propylene.) Also of interest is the appearance of a feature near 1342 cm^{-1}, and a shift similar to that observed in the ethylene spectra of the feature at 3669 cm^{-1} (at 300 K) to 3625 cm^{-1} (575 K).

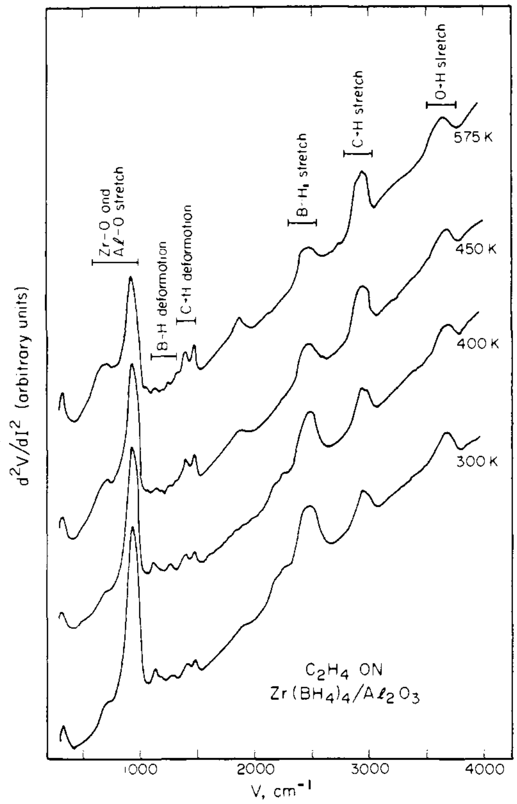

Figure 1. IET spectra (240-4000 cm^{-1}) for saturation coverages of ethylene on $Zr(BH_4)_4/Al_2O_3$ at 300, 400, 450, and 575 K.

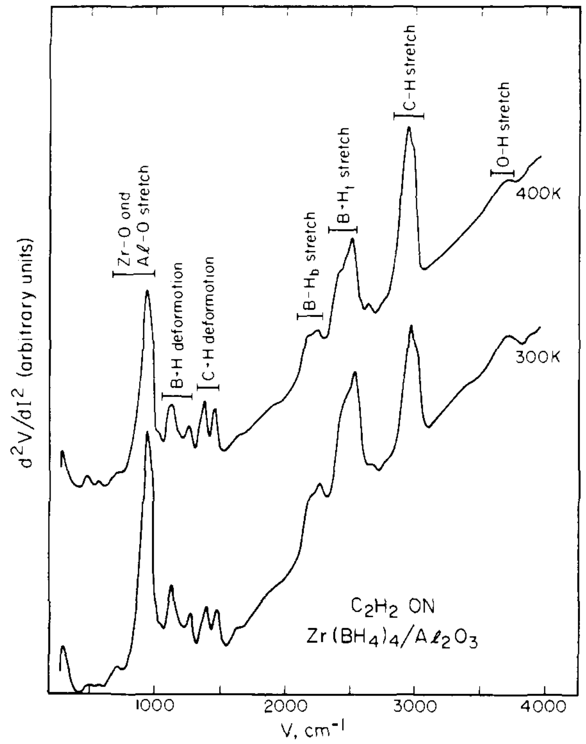

Figure 2. IET spectra for saturation coverages of propylene on $Zr(BH_4)_4/Al_2O_3$ at 300, 400, and 575 K.

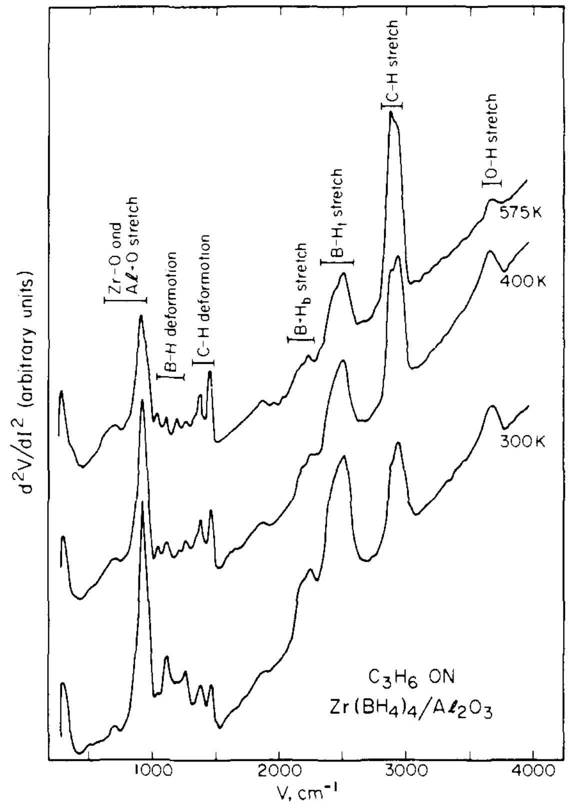

Figure 3. IET spectra of acetylene (300 Torr s exposure) on $Zr(BH_4)_4/Al_2O_3$ at 300 and 400 K.

Acetylene adsorption exhibited different behavior than either ethylene or propylene. Spectra for 3×10^2 Torr s exposure of acetylene at 300 and 400 K are shown in Figure 3. At higher temperatures, the concentration of hydrocarbon species on the surface increased rapidly *with no apparent saturation limit.* Hydrocarbon concentration can be monitored approximately by measuring the resistance of the aluminum oxide plus adsorbed species insulating layer between the Al and Pb electrodes. Samples producing usable spectra typically fall in the 30-200-Ω range (for an area of approximately 1 mm^2), since these exhibit the best signal/noise ratios utilizing our electronics. The thickness of the oxide layer can be controlled by varying the O_2 plasma discharge parameters (principally time), and the resistance of samples with various adsorbate concentrations can thus be adjusted to fall within this range. No samples with acetylene exposures above 400 K could be prepared with resistance below several kilohms. (Exposures, unfortunately, could not be reduced below 5 Torr s using our current pressure monitoring system.) The intensity of the features in the 2850-3000-cm^{-1} region for acetylene is comparable to that observed for propylene and significantly greater than that observed for ethylene. Intensity decreases in the 1100-1250-, 2150-2300-, and 2400-2500-cm^{-1} regions are not so great for acetylene exposures as for the other two hydrocarbons. Structure in the 2400-2500-cm^{-1} region is similar in appearance to that observed for propylene, the most prominent feature being a peak at 2505 cm^{-1} (at 300 K). A peak at 2978 cm^{-1} is approximately 20 cm^{-1} higher in energy than corresponding features for ethylene and propylene. There is a small feature appearing near 1351 cm^{-1}, which possibly corresponds to features near 1302 and 1342 cm^{-1} for ethylene and propylene, respectively. Two well-resolved peaks can be seen at 485 and 573 cm^{-1}. Although there is weak structure in the 480-580-cm^{-1} region for both ethylene and propylene, it is weaker than for acetylene and cannot be resolved clearly. A weak feature is present near 1613 cm^{-1}. No shift of the 3677-cm^{-1} peak with temperature is observed, although this is to be expected since shifts observed for this peak in the spectra of adsorbed ethylene and propylene were not continuous and appeared only at higher temperatures.

It should be reiterated that hydrocarbon adsorption was not observed for exposures of acetylene, ethylene, or propylene to aluminum oxide surfaces with no preadsorbed $Zr(BH_4)_4$. This is in agreement with a previous IR study which also failed to observe ethylene or propylene adsorption on alumina.[11] No hydrocarbon contamination is observed for "clean" Al_2O_3 surfaces. The amount of contamination observed on the supported complex without deliberate exposure to hydrocarbons can be observed in previously published spectra.[1]

Discussion

A. Supported Zirconium Tetraborohydride. Figure 1 in the preceding paper shows the spectrum of $Zr(BH_4)_4$ supported on Al_2O_3 at 300 K, together with a listing of observed peak positions. This spectrum has been analyzed in detail.[1] At least two discrete types of surface zirconium species were observed (i.e., with zirconium atoms being singly or multiply coordinated to surface oxygens), together with AlH_2BH_2 and OBH_2 species formed by the migration of displaced BH_4 ligands onto the Al_2O_3.

B. Nature of Polymerization Reaction. Unsaturated hydrocarbons can be expected to interact with many, if not all, of the various types of surface species formed during $Zr(BH_4)_4$ adsorption. This has been confirmed for the AlH_2BH_2 and OBH_2 species in a study of olefins interacting with adsorbed diborane.[11] Supported zirconium complexes, particularly those supported on Al_2O_3, are known to be active for the polymerization of olefins. Group 8 transition metals, on the other hand, readily form complexes with olefins but make poor polymerization catalysts. This difference in polymerization activity between zirconium and group 8 metals is attributed to the weaker interaction of olefins with zirconium.[5] Zirconium has few, if any (depending on the oxidation state), d electrons for back-donation to olefins. Therefore, only a relatively weak Lewis acid-Lewis base type interaction occurs. (Zr^{4+} has been observed in other studies to function as a strong Lewis acid.[3]) This type of interaction allows for the formation of π complexes as olefins become coordinated nonlinearly to zirconium atoms. This coordination, without displacing additional ligands from the supported complex, is generally considered to be the first step in the polymerization process. The next step is insertion of the hydrocarbon between the zirconium atom and one of its remaining ligands. Repeated coordination and insertion of other olefin molecules create a polymer chain. It has been postulated that only hydrogen ligands form active centers for polymerization.[5] BH_4 groups could also have several functions in such a reaction scheme, e.g., providing a source of hydrogen (forming Zr-H active centers), providing a variable coordination sphere for the zirconium, or exerting some activating influence on other ligands.

C. Polymer Formation and Hydrocarbon Adsorption. The observed behavior of acetylene exposed to $Zr(BH_4)_4/Al_2O_3$ can be explained consistently by the formation of polyacetylene on the surface. There are no corresponding definite indications of polymer formation resulting from ethylene and propylene exposures. The conclusions are based partly on the observed adsorption characteristics and also on comparisons of the vibrational spectra observed here to published results for saturated and unsaturated hydrocarbons,[12,13] polyethylene,[14-17] polypropylene,[17-19] and polyacetylene.[20]

The polymerization of acetylene is of significant interest and importance owing to the recently discovered electrical conductivity properties of doped polyacetylenes (see, for example, ref 21 and 22 and references cited therein). Perhaps the most obvious indication of polymer formation in the case of acetylene is its continuous adsorption without reaching saturation coverage under the exposure/temperature conditions studied here. On the other hand, the observed rapid attainment of saturation coverages for ethylene and propylene indicates no extensive formation of polymers on the surface. It is possible that conditions are such as to foster only the growth of short chains, which undergo frequent separation from the surface via hydrogenolysis. More likely is a lack of polymerization centers which are sufficiently active to promote continued reaction under the conditions which we employed. High surface concentrations of zirconium complexes might be a factor (as discussed above), with coordination of even a limited number of olefins creating steric barriers preventing further olefin coordination at the active centers. The observed slight increase in hydrocarbon concentration with temperature would then occur as a few new active centers (Zr-H) are formed, or as some olefin molecules become energetic enough to displace BH ligands or overcome steric effects which previously blocked active sites.

D. Adsorbed C_2H_4 and C_3H_6. Analysis of the hydrocarbon stretching and deformation modes can be expected to yield information about the nature of the various surface species. The fact that many different types of CH groups can produce peaks in similar spectral areas definitely complicates interpretation of the spectra. As noted above, the interpretations and conclusions presented here are those which appear to reflect all of the observed data in the most consistent manner, although other interpretations might be possible. A more detailed view than is available in the other figures of the spectral region between 2000 and 3300 cm^{-1} is shown in Figure 4. This includes the C-H stretching region (2850-3000 cm^{-1}), and compares spectra of ethylene, acetylene, and propylene exposed to the supported complex at 300 K. Although more than one type of surface species might be expected owing to the inhomogeneity of the $Zr(BH_4)_4/Al_2O_3$ surface, the number of observed C-H stretching modes (four each for ethylene and propylene, two plus a possible weak shoulder for acetylene) is inconclusive in determining the number of possible surface hydrocarbon species. For example, up to four distinct modes can be observed for a single type of saturated hydrocarbon containing both CH_2 and CH_3 groups, while, alternately, degeneracies and loss of distinct structure due to inadequate resolution of closely spaced features can lead to fewer observed peaks for other molecules which also contain CH_2 and CH_3 functional groups.[12] More definite information can be expected from examining the peak positions. Surface species formed from ethylene and propylene are saturated hydrocarbons as judged from the absence of a C=C stretch near 1600 cm^{-1}. This is also expected based on the postulated adsorption mechanism of insertion as discussed above. (Insertion reactions can occur with the aluminum borohydride and OBH_2 species, as well as with zirconium complexes.) C-H stretching features (a combination of both CH_3 and CH_2) would thus be anticipated between approximately 2860 and 2960 cm^{-1}, with corresponding deformation modes near 1450, 1375, and 1350-1150 cm^{-1}.[12] This correlates well with features observed at 2879-2960, 1455, 1383, and 1302 cm^{-1} for ethylene and at 2863-2952, 1449, 1378, and 1342 cm^{-1} for propylene.

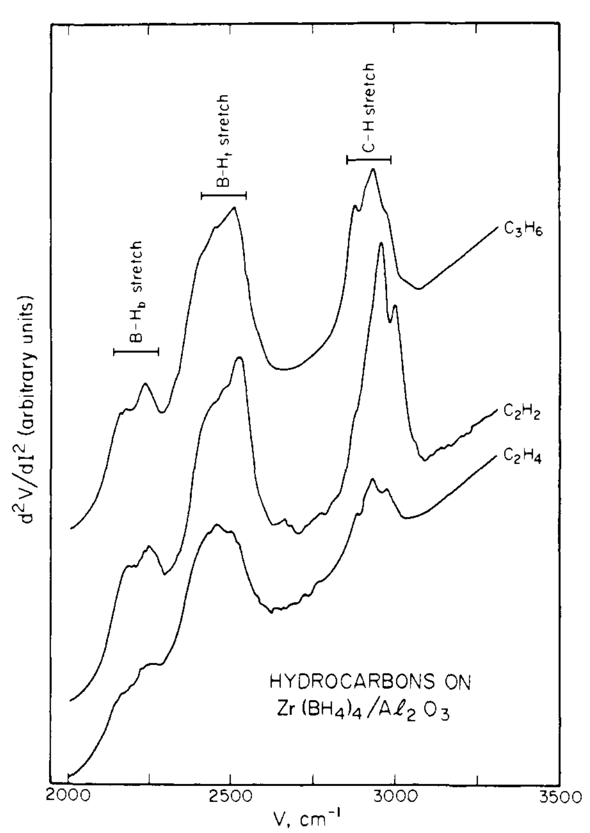

Figure 4. Comparative view of the BH (2000-2500 cm^{-1}) and CH (2850-3000 cm^{-1}) stretching features in the IET spectra for ethylene, acetylene, and propylene on $Zr(BH_4)_4/Al_2O_3$ at 300 K.

E. Polyacetylene. Polyacetylene has a conjugated double bond skeletal structure as shown:

$$-C=C-C=C-C=C-$$

each carbon atom along the chain being attached to a single hydrogen.[20] Polymer formed here by acetylene adsorption on $Zr(BH_4)_4/Al_2O_3$ might consist of relatively short or highly branched chains, or might have a double bond:single bond ratio less than one (i.e., imperfections in the conjugated skeletal structure). Such situations could lead to a nonnegligible population of $-CH_2-$ and/or $=CH_2$ groups which would also contribute to the observed spectra. (Formation of CH_3 groups is unlikely as they would require a significant source of hydrogen.) The presence of some unconjugated C=C bonds is indicated by a possible weak feature at 1597 cm^{-1} (C=C stretch). The conjugated polymer chain has been shown to have a carbon–carbon stretching feature near 1370 cm^{-1}, indicative of an interaction intermediate between that of a single bond (900–1000 cm^{-1}) and that of a double bond (1600–1700 cm^{-1}).[20] A feature appearing in our acetylene spectra at 1380 cm^{-1} can thus be assigned to a carbon–carbon stretching mode of polyacetylene. The observed C—H stretching peaks also exhibit some degree of unsaturation, being higher in energy than saturated species, but lower than for pure C=C or C≡C bonded molecules. Polymer chains have been observed to have skeletal deformation modes between 400 and 600 cm^{-1}, these modes being particularly evident if unsaturated linkages occur within the chain.[19] Spectra of adsorbed acetylene show two well-resolved peaks at 485 and 573 cm^{-1}. This is in marked contrast to the low-intensity, unresolved structure appearing in the 480–580-cm^{-1} region due to Zr–O and Zr–BH$_4$ modes. These observations are consistent with the identification of acetylene polymer.

F. Borohydride Ligands. An examination of Figure 4 reveals perturbations of B–H$_t$ stretching modes caused by hydrocarbon adsorption. Ethylene adsorption appears to reduce intensity around 2490 cm^{-1}, while having less effect on other features in the 2400–2500-cm^{-1} region. Acetylene and to a lesser extent propylene have just the opposite effect on B–H$_t$ stretching modes: their adsorption greatly strengthens structure at 2500 cm^{-1}. The basis for these varying effects on B–H$_t$ vibrations is as yet unclear. It is also of interest to note that in the case of acetylene a high surface concentration of hydrocarbon can accumulate with very little (if any) accompanying loss of BH groups. This is consistent with the view that polymer formation at a few active centers (probably Zr–H) is the mechanism for incorporating additional acetylene molecules into the surface phase.

Conclusions

Various aspects concerning the interactions of unsaturated hydrocarbons with supported zirconium complexes are revealed in the vibrational spectra of Zr(BH$_4$)$_4$/Al$_2$O$_3$ samples exposed to ethylene, propylene, and acetylene.

By analyzing both the positions and shapes of features in the C–H stretching region (2850–3000 cm^{-1}), it is observed that ethylene and propylene both saturate upon adsorption, forming surface species with similar types of -CH$_3$ and -CH$_2$- groups. Surface acetylene structures are somewhat different, probably consisting mainly of -CH- and -CH$_2$ groups while retaining some characteristics of unsaturated carbon–carbon bonds. Ethylene and propylene readily saturate the surface with no indication of polymer formation under the conditions studied here. Only slight increases in surface concentration occur with temperature up to 575 K. Acetylene, however, does appear to polymerize on the surface. Saturation coverages are apparently not obtained within the observed temperature and exposure ranges. High concentrations of surface hydrocarbons are obtained with little or no effect on the concentration of BH species, since acetylene apparently forms long polymer complexes from a small number of active centers (probably Zr–H) without displacing existing ligands. The identification of acetylene polymer is supported by two well-defined peaks at 485 and 573 cm^{-1} characteristic of polymer skeletal deformations. A peak at 1380 cm^{-1} can be assigned to a C–C stretch whose bond strength is intermediate between that of a single and of a double carbon–carbon bond, as observed in an IR study of bulk polyacetylene.[20] This study of hydrocarbons interacting with supported zirconium complexes further demonstrates the versatility and value of IETS by providing important, new data on a unique catalytic system of significant industrial as well as fundamental importance.

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