(m, 1 H), 3.64 (s, 3 H), 3.20–3.45 (m, 2 H), 3.30 (s, 3 H), 2.67 (br t, $J = 6$ Hz, 2 H), 1.50 (s, 9 H), 1.18 (d, $J = 6$ Hz, 3 H).

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Inelastic Electron Tunneling Spectroscopy of Zirconium Tetraborohydride Supported on Aluminum Oxide

Sir:

Currently, there is significant interest in newly developed supported-complex catalysts, which are formed by anchoring or grafting a homogeneous catalyst (a cluster compound) onto a high surface area support.[1] Such catalysts can combine the activity and selectivity found in homogeneous systems with the stability and ease of separation characteristic of heterogeneous catalysts, and they frequently exhibit activities an order of magnitude or more greater than the corresponding unsupported systems.[2] Progress in this area, however, has been hampered by a lack of detailed structural information for supported complexes. Characterization of supported complexes has been poor, plagued by many of the same problems that arise in attempting to characterize traditional heterogeneous catalysts; and, as yet, there are not reported cases where the structure of a supported complex has been definitely determined, at least employing vibrational spectroscopy. We report here the vibrational spectrum of the supported complex formed by the interaction of zirconium tetraborohydride, $Zr(BH_4)_4$, a known homogeneous polymerization catalyst for olefins, with an alumina surface. This vibrational information was obtained utilizing inelastic electron tunneling spectroscopy (IETS).

IETS involves monitoring the current due to electrons tunneling inelastically through a thin insulating barrier between two metal electrodes. Although most of this tunneling current is elastic, some electrons can tunnel inelastically by exciting vibrational modes of molecules at, or near, the surface of the insulating barrier. Such inelastic transitions can occur only when the bias voltage across the barrier is greater than, or equal to, a vibrational excitation energy, and lead to increases in conductance across the barrier by providing additional channels for electron tunneling. These conductance increases become peaks when the second derivative of voltage with respect to current, d^2V/dI^2 (proportional to d^2I/dV^2), is plotted as a function of the bias voltage, V. Peak positions correspond to vibrational excitation energies and yield information analogous to that obtained by optical absorption spectroscopies. Both IR and Raman active modes are observed in the IET spectra. Further theoretical and experimental details are available elsewhere.[3]

In our experiments, the top few atomic layers of a freshly evaporated Al film were oxidized to form the thin insulating barrier. The $Zr(BH_4)_4$ was then allowed to adsorb on the resultant aluminum oxide surface. Saturation coverage was obtained by exposure to 5×10^{-2} Torr of $Zr(BH_4)_4$ for 15 min. The samples were completed by evaporation of top metal (Pb) electrode. Measurements were made over the entire spectral range from 240 to 4000 cm^{-1}, with a resolution on the order of 4 cm^{-1} and a sample surface area of ~1 mm^2. An IET spectrum for a saturation coverage of $Zr(BH_4)_4$ on aluminum oxide at 300 K is shown in Figure 1. Peak positions are also indicated in the figure.

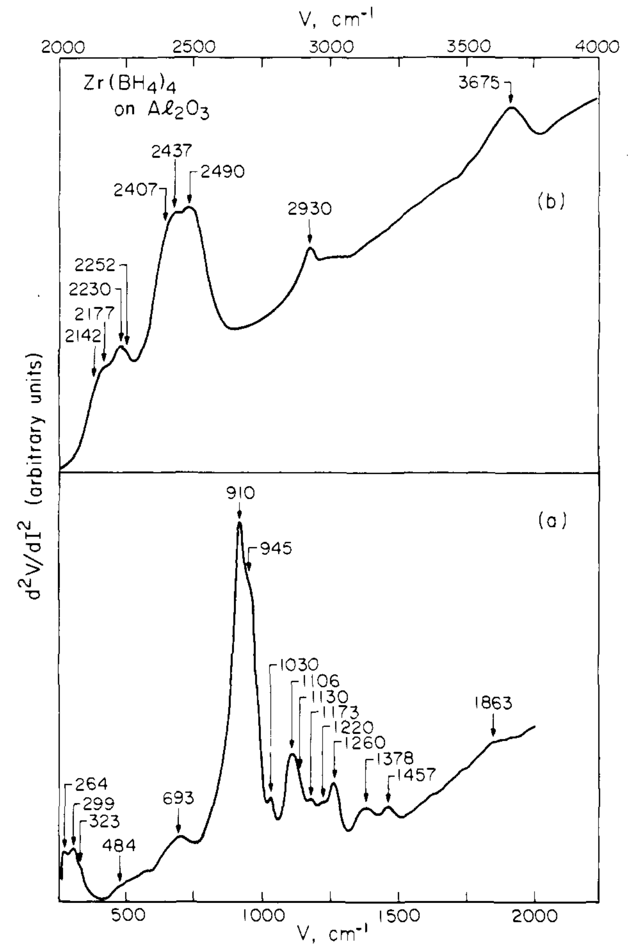

Figure 1. IET spectrum for $Zr(BH_4)_4$ supported on Al_2O_3 at 300 K over the energy range (a) 240–2000 cm^{-1} and (b) 2000-4000 cm^{-1}.

Comparisons with IETS studies of "clean" Al_2O_3 indicate that the spectral features at 299, 945, and 1863 cm^{-1} can be assigned to a phonon in the underlying Al film, a bulk Al-O stretching mode, and its harmonic overtone, respectively.[4] The 3675-cm^{-1} peak is the O-H stretching vibration of surface hydroxyl groups, while the peak near 2930 cm^{-1} arises from the C-H stretching vibration of a small amount of adsorbed hydrocarbon contamination.[4] Contamination might also contribute to the intensity of features at 1030 cm^{-1} and in the 1300-1500-cm^{-1} region.

The boron atoms in $Zr(BH_4)_4$ are arranged tetrahedrally, each being bound to the central Zr atom in a tridentate manner with three bridging hydrogens.[5] During adsorption, one or more of the BH_4 ligands are lost as the Zr becomes either singly or multiply coordinated to oxygen atoms on the surface.[2] Since the surface becomes a virtual ligand, it might well affect bonding in the remaining BH_4 groups. For example, $(C_5H_5)_2Zr(BH_4)_2$ and $(C_5H_5)_2Zr(H)BH_4$ are both known to have bidentate bridging structures,[6] and the surface could be expected to have a similar effect. Information concerning bonding can be obtained by examining the stretching vibrations of both terminal (H_t) and bridging (H_b) hydrogens. The B-H_t region shows at least three peaks near 2407, 2437, and 2490 cm^{-1}. For the tridentate structure, only one (possibly broadened) peak at 2560-2580 cm^{-1} is to be expected.[7] The observed frequencies are more closely related to those reported

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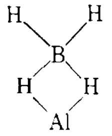
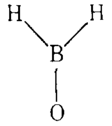
for bidentate species (between 2375 and 2550 cm^{-1});[6] yet the presence of more than two peaks, as well as the observation of four features in the $B-H_b$ stretching region (at 2142, 2177, 2230, and 2252 cm^{-1}), indicates that there is either more than one type of surface species or strong intramolecular vibrational coupling among BH_4 groups attached to the same Zr atom. The former explanation is consistent with the assignments of features at 693 and 910 cm^{-1} to Zr-O stretching modes of multiply (bulk-like) and singly (or, at least, less highly) coordinated Zr atoms.[8,9] Additionally, some of the BH_4 ligands displaced during adsorption might remain on the surface, forming complexes A and B. Similar surface species have been observed for diborane (B_2H_6) adsorption on Al_2O_3[10] and could also be expected to produce additional structure in the B-H stretching regions. Modes appearing at 1106, 1130, 1173, 1220, and 1260 cm^{-1} (and possibly 1030 cm^{-1}) can be assigned to deformations of the metal-BH_4 structure.[7] An AlH_2BH_2 deformation might also contribute to structure near 1457 cm^{-1}.[10] The 1378-cm^{-1} peak has been previously assigned to a B-O stretch, and a B-O vibration might also contribute to the intensity of the 1260-cm^{-1} peak.[10] Unresolved structure between 480 and 600 cm^{-1} can be assigned to Zr-B skeletal stretching modes,[11] with possible contributions from additional Zr-O vibrations.[8] Low energy features near 264 and 323 cm^{-1} probably arise from BH_4-Zr-BH_4 bending and Zr-BH_4 torsional modes.[7]



A



B

Although this is by no means a complete characterization of alumina-supported $Zr(BH_4)_4$ (the details of more extension results characterizing the supported complex as a function of temperature, as well as its interaction with D_2, D_2O, H_2O, C_2H_4, C_3H_6, and C_2H_2 will be reported later), this preliminary communication does indicate the versatility of IETS and clearly demonstrates the value of information that can be obtained by applying IETS to the study of supported complexes. This work represents an important extension of IETS beyond the study of adsorption either on oxide surfaces[3] or on reduced metallic particles evaporated onto oxide supports.[12-15]

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Enhanced CD Spectra in *cis*-Bis(nucleotide)platinum(II) Complexes. Comparison with the CD Enhancement Induced in DNA by the Anti-Tumor Agent, *cis*Pt

Sir:

We have observed a marked enhancement of the CD spectrum of 5′-GMP or 5′-dGMP on coordination of two molecules of either nucleotide to cis positions of complexes which are derivatives of *cis*Pt (≡*cis*$Pt^{II}(NH_3)_2Cl_2$).[1] The latter species is gaining widespread clinical use as an anti-tumor agent.[2] After assessing numerous biological and biochemical studies on *cis*Pt, Roberts and Thomson[3] have concluded that DNA is the important molecular target for the anti-tumor activity of *cis*Pt and have suggested that the effective interaction of *cis*Pt with DNA is an intrastrand cross-link. Numerous lines of evidence indicate that guanosine moieties in DNA are attacked first by Pt(II) complexes such as *cis*Pt[4] when Pt/DNA ratios are low. Several studies on small molecules, the first of which was on bis(guanosine)ethylenediamineplatinum(II) nitrate,[5] verify that two adjacent guanine bases can coordinate to Pt(II) via N-7.[4] Other lines of evidence demonstrate that intrastrand cross-linking between adjacent guanosine moieties does occur in Pt-DNA.[6] However, a clear structural relationship between well-defined N-7-bound *cis*-bis(6-oxopurine)platinum(II) complexes and the possible intrastrand cross-link has not been established because of the difficulty involved in either crystallizing nucleic acids or of obtaining NMR spectra on Pt-DNA.[1]

A dramatic effect of low concentrations of *cis*Pt on the CD of polynucleotides was reported by Eichhorn and his coworkers[7,8] and later confirmed by others.[9] At low Pt/base ratios, there is a marked enhancement in the CD spectrum of the polynucleotide and, for calf thymus DNA, there is a positive increase in the CD at ~275 nm. No such effect is observed for the trans isomer of *cis*Pt[7,8] (or for other Pt(II) complexes which do not have cis leaving groups[9]). The trans isomer is not an anti-tumor agent. The magnitude of the enhancement [$(\epsilon_L - \epsilon_R) \sim 5$-$7.5\ M^{-1}\ cm^{-1}$ per mole of affected nucleotide] increases with increasing GC content of the polynucleotide.[8,9] The guanosine moieties are probably playing a role in the enhancement.

In Figure 1, we present the CD spectrum of the complex sodium bis(5′-GMP)tnPt^{II}. The maximum at 284 nm has a value of $(\epsilon_L - \epsilon_R)$ 4.6 $M^{-1}\ cm^{-1}$ per nucleotide. The strength of this band closely approximates the magnitude of the effect of *cis*Pt and other Pt(II) compounds with cis leaving groups on the CD of DNA in the 275-nm region of DNA, when allowance is made for the low Pt/base ratios used to observe the enhanced CD.

The two tn complexes, for which spectra are presented in Figure 1, were obtained as microcrystalline powders and were characterized by ^1H and ^{13}C NMR (Table I), by UV as well as CD spectroscopy (Table II), and by elemental analysis (Table I). The shift pattern obtained for resonances assignable to the heterocyclic ring closely resembles that found for Pt(II)