

Summary Abstract: Synthesis and catalytic reactions of $Zr(BH_4)_4$ on Al_2O_3 characterized by inelastic electron tunneling spectroscopy

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Currently, there is significant interest in newly developed supported-complex catalysts, which are formed by anchoring known homogeneous catalytic compounds onto high surface area support materials.¹ Such catalysts can combine the activity and selectivity found in homogeneous systems with the stability and ease of separation from products 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. Indeed, no definite proof of any structure for such a complex has heretofore been reported. In the current work, inelastic electron tunneling spectroscopy (IETS) has been utilized to probe vibrational structure of $Zr(BH_4)_4$ (zirconium tetraborohydride, a tetrahedral molecule in the gas phase) adsorbed on aluminum oxide. IETS has been shown to be an effective means of characterizing the vibrational structures of molecules near insulating surfaces, and both the theoretical and experimental aspects of IETS have been detailed elsewhere.³ Metal borohydride compounds, such as $Zr(BH_4)_4$, have been of considerable interest due both to the unique types of M-H-B bonds existing in such molecules and, more importantly, due to their ability to catalyze polymerization reactions of unsaturated hydrocarbons. The nature of the supported zirconium complex has been determined by investigating its behavior as a function of temperature from 300 to 475 K and also its interactions with D_2 , D_2O and H_2O . Additionally, results have been obtained for C_2H_2 , C_2H_4 and C_3H_6 on alumina-supported $Zr(BH_4)_4$.

Figure 1 shows the spectrum of $Zr(BH_4)_4$ on Al_2O_3 at 300 K, together with a listing of observed peak positions. Features at 910 and 693 cm^{-1} have been assigned to Zr atoms singly and multiply coordinated to surface oxygen atoms, respectively. An analysis of the BH stretching frequencies (2140–2500 cm^{-1} , in particular the structure between 2142 and 2152 cm^{-1}) indicates that boron atoms are bonded to zirconium atoms through two bridging hydrogens (bidentate bonds) in the supported complex, as opposed to the tridentate bonding (three bridging hydrogens) that occurs in pure $Zr(BH_4)_4$. Some BH_4 groups displaced during adsorption migrate onto the alumina, forming AlH_2BH_2 and OBH_2 species.⁴ Boron-oxygen vibrations are observed in the 1250–1460 cm^{-1} region.

The surface species formed from ethylene and propylene adsorbed on the supported complex are saturated hydrocar-

bons as judged from the absence of a C=C stretch near 1600 cm^{-1} . CH stretching frequencies between 2860–2960 cm^{-1} also correlate well with the identification of completely saturated species. The fact that saturation coverages of ethylene and propylene are readily obtained indicates that little polymerization is occurring on the surface under the low-pressure conditions employed here. Acetylene, however, can be adsorbed on the surface with no apparent saturation limit, which is indicative of extensive polymer formation. The formation of polyacetylene, which is known to have a con-

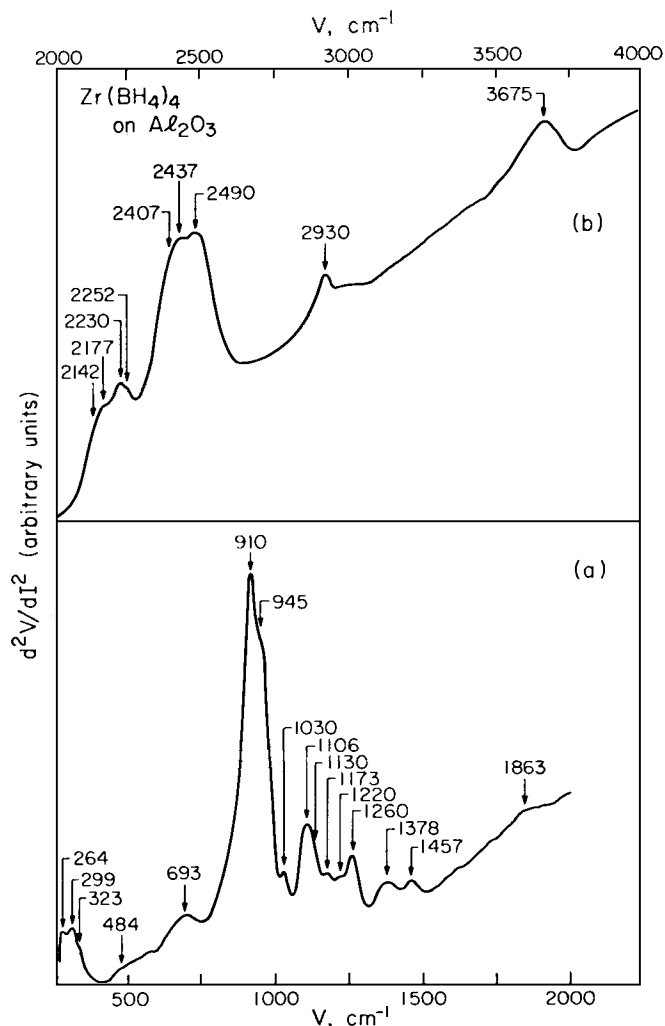


FIG. 1. IET spectra of $Zr(BH_4)_4$ adsorbed on Al_2O_3 at 300 K over the spectral ranges: (a) 240–2000 cm^{-1} and (b) 2000–4000 cm^{-1} .

jugated double bond skeletal structure, is supported by CH and CC stretching frequencies indicative of such bonding,⁵ as well as by the appearance of well-defined peaks at 485 and 573 cm^{-1} which can be identified as skeletal modes of polymer chains.⁶

This study of supported $\text{Zr}(\text{BH}_4)_4$ and its interactions with unsaturated hydrocarbons not only demonstrates further the value and versatility of IETS, but also provides important new data on a unique catalytic system of significant industrial as well as fundamental importance.

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