

Summary Abstract: Vibrational study of $Zr(BH_4)_4$ supported on alumina: Interactions with cyclohexene, 1,3-cyclohexadiene, and benzene^{a)}

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Inelastic electron tunneling spectroscopy (IETS)¹⁻³ has been used to investigate the interactions of the known polymerization catalyst, $Zr(BH_4)_4$ supported on Al_2O_3 , with cyclohexene, 1,3-cyclohexadiene and benzene. Results of the interactions of the $Zr(BH_4)_4$ catalyst with the Al_2O_3 support itself, and with the supported $Zr(BH_4)_4$ exposed to D_2 , D_2O , H_2O , ethylene, propylene and acetylene have been reported previously.⁴⁻⁶ A particularly significant result of these previous studies was the observation that polymer formation occurred upon interaction of the supported $Zr(BH_4)_4$ with acetylene at elevated temperatures.

The IET junctions used in this study were prepared using standard procedures which are reported elsewhere.⁴⁻⁶

Figure 1 shows the vibrational spectra of the supported $Zr(BH_4)_4$ catalytic system after exposure to benzene, 1,3-cyclohexadiene, and cyclohexene at 300 K. Features associated with the support surface are the Al phonon at 299 cm^{-1} , the Al-O (bulk) stretch at 945 cm^{-1} , its first overtone near 1865 cm^{-1} , and the OH stretch of surface hydroxyl groups near 3650 cm^{-1} . Features due to the supported $Zr(BH_4)_4$ catalyst are Zr-O modes near 690 and 910 cm^{-1} , BH_4 deformation modes between 1000 and 1300 cm^{-1} , stretching of bridging hydrogens in BH_4 ligands (B-H_b) between 2100 and 2300 cm^{-1} , and stretching of terminal hydrogens in BH_4 li-

gands (B-H_t) between 2400 and 2600 cm^{-1} . B-O modes due to disassociated BH_4 ligands which form surface complexes rather than desorbing when $Zr(BH_4)_4$ adsorbs on the Al_2O_3 substrate are expected between 1200 and 1450 cm^{-1} .⁷ Hydrocarbon deformation modes appear between 1000 and 1500 cm^{-1} and hydrocarbon stretching modes between 2850 and 3050 cm^{-1} .

A comparison of the spectra in Fig. 1 reveals that cyclohexene appears to perturb the supported catalyst less than the other two adsorbates as based on the relative intensities of the features in the B-H_b and B-H_t regions and the hydrocarbon stretching region also appears to be more intense than in the other two spectra. However, 1,3-cyclohexadiene, and to a much lesser extent benzene, appear to interact with the supported $Zr(BH_4)_4$ catalyst primarily by displacement of BH_4 ligands as evidenced by the greatly reduced intensity of the B-H stretching features. The spectra reveal that this displacement occurs readily even at room temperature when 1,3-cyclohexadiene is the adsorbate. Previous studies indicate that ethylene, propylene and acetylene do not appear to displace BH_4 ligands readily at 300 K.⁶

The vibrational spectra of the supported $Zr(BH_4)_4$ catalyst after exposure to cyclohexene at 300, 400, and 480 K are shown in Fig. 2 for the spectral range of 2000 to 4000 cm^{-1} .

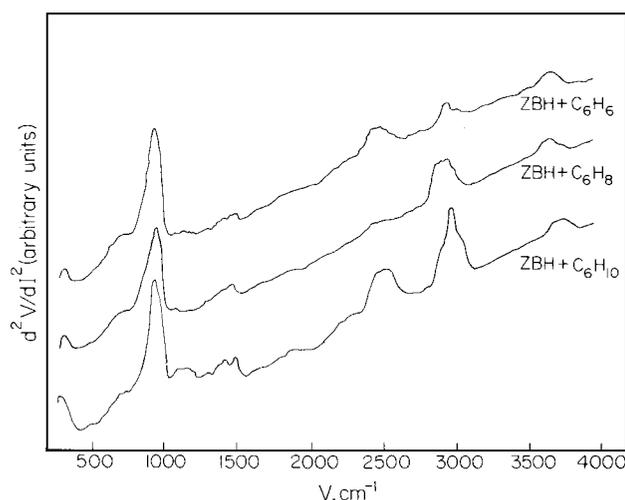


FIG. 1. IET spectra ($240\text{--}4000\text{ cm}^{-1}$) of cyclohexene (C_6H_{10}), 1,3-cyclohexadiene (C_6H_8), and benzene (C_6H_6) on $Zr(BH_4)_4/Al_2O_3$ (ZBH) at 300 K.

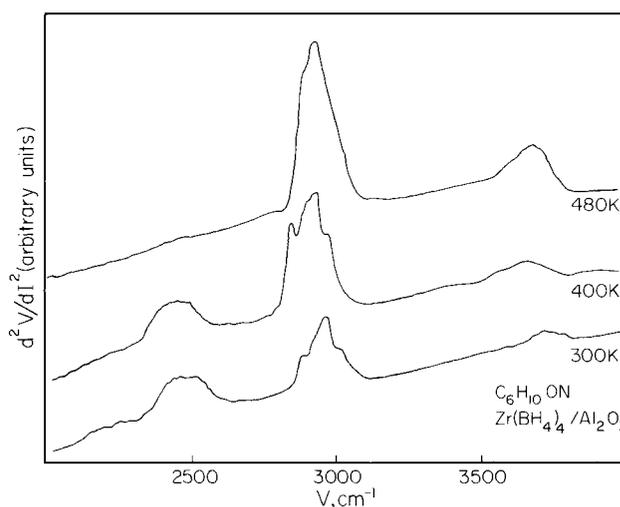


FIG. 2. IET spectra ($2000\text{--}4000\text{ cm}^{-1}$) of cyclohexene on $Zr(BH_4)_4/Al_2O_3$ at 300, 400, and 480 K.

At 400 K, the B-H stretching regions are reduced in intensity and the C-H stretching region is much more intense, indicating a greater amount of adsorbed hydrocarbon. The number of hydrocarbon stretching modes at 300 and 400 K indicates that there may be more than one type of surface hydrocarbon species present. There is also a slight shift to lower frequencies upon heating. Upon heating to 480 K, a significant transformation of the surface species occurs. The B-H_i stretching features have virtually disappeared and only an extremely weak feature remains in the B-H_t region, indicating that the majority of the BH₄ ligands have been displaced from the Zr centers. The hydrocarbon stretching feature indicates that the surface species formed at this temperature is quite uniform as evidenced by the disappearance of multiple stretching features found at lower temperatures and the appearance of one major peak with an unresolved shoulder at slightly lower frequency. The spectral features indicate the surface complex formed at 480 K may be a Zr-alkyl complex resulting from the hydrogenation of the cyclohexene. Previous studies have shown that zirconium hy-

drides are catalysts for the hydrogenation of olefins, including cyclohexene.⁸

Future IETS studies of other supported polymerization catalysts will undoubtedly yield further information on the exciting surface chemistry of these industrially important catalysts.

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