289an A Solid State NMR Study of the Surface Reaction of the Supported Palladium Catalyzed Hydrodechlorination of Trichloroethylene

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This study utilized ^{13}C and ^{35}Cl solid state NMR to elucidate the mechanism of the surface catalyzed reductive dechlorination reaction of trichloroethylene (TCE) on alumina supported palladium catalysts (Pd/Al_2O_3). The first part of this research involved adsorption of ^{13}C-enriched TCE to identify the surface species that form when TCE interacts with the Pd surface. In the second part, TCE and hydrogen were coadsorbed to discover the intermediates and products that form during Pd catalyzed reductive dechlorination. Results from ^{13}C NMR spectra of TCE adsorbed on Pd/Al_2O_3 at room temperature showed that there are two types of strongly chemisorbed carbon species. Measurements of the ^{13}C-^{13}C dipolar coupling were used to determine the carbon-carbon bond length of adsorbed species. Approximately 60% of the chemisorbed carbon species possess an elongated carbon-carbon bond with a length of 1.46±0.02 Å and are likely an ethynyl (CCH) bonded to Pd. The second type of chemisorbed carbon species that was identified consisted of carbon fragments adsorbed on the Pd clusters. This suggests that the activation energy for carbon-carbon bond scission is quite low and is comparable to the heat of adsorption. Chlorine-35 NMR data supports the hypothesis that chlorine atoms are also strongly chemisorbed onto the metal clusters. When hydrogen is coadsorbed with ^{13}C-TCE on Pd/Al_2O_3, ethane is the dominant product. Chlorinated single carbon intermediates react to form methane but only slowly (on the order of months) and only with excess hydrogen. When enough hydrogen is present, ethynyl is no longer observed , presumably because it reacts to ethane. Reaction of TCE and hydrogen was observed with ^{13}C NMR as the temperature changes from 77K to 292K. The formation of the carbon fragments as well as ethane was observed at temperatures as low as 215 K. At 273 K, ethane formation was almost complete. However, when TCE is pre-adsorbed at room temperature, no formation of ethane was observed until the sample was at 292 K. Taken together, NMR data indicate that the most reactive intermediate is physisorbed TCE. The newly discovered chemisorbed ethynyl and single-carbon fragments are relatively stable and react slowly to ethane and methane, respectively.