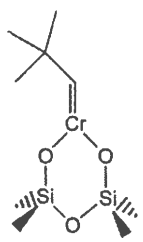
Structure and Reactivity of Silica-Bound Transition Metal Akylidenes and Hydrides

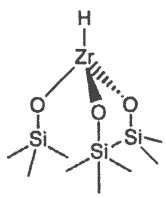
Paul W. Dickinson Literature Seminar December 9, 1999

Heterogeneous catalysts used industrially often suffer from several drawbacks: notably, they tend to have relatively poor activity and poor selectivity. These drawbacks are consequences of the inherent variety of sites found in most catalysts. For a given catalyst, only one type of site may catalyze the desired reaction. At best, the other sites are inactive and, at worst, they catalyze side reactions. Despite intensive study, the active site is usually unknown for most catalysts, making a molecular level understanding of its activity difficult. Without this understanding, modifying the catalyst to improve activity and selectivity based on molecular concepts becomes virtually impossible.

The grafting of organometallic compounds onto surfaces is one of the strategies employed in the rapidly developing field of surface organometallic chemistry. One of the goals of surface organometallic chemistry is the synthesis and characterization of well-defined heterogeneous catalysts. By grafting onto surfaces certain organometallic compounds that then may act as catalytically active sites (or may be the precursors for catalytically active sites), the problem of diversified sites is eliminated and often the active site can be understood on a molecular level. This approach makes modification of the catalyst based on molecular concepts a much more feasible endeavor. Three such systems recently synthesized and studied are a silica-bound chromium neopentylidene, a silica-bound zirconium monohydride, and a silica-bound tantalum monohydride.



I



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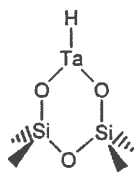

III

Sublimation of tetraneopentylchromium ($CrNp_4$) onto a pyrogenic silica previously dehydrated at 200°C forms a product that consists of discrete Cr^{IV} dineopentyl units bound to the silica surface. When this product is heated at 69°C for 10 hours, one equivalent of neopentane is liberated and a silica-bound Cr^{IV} neopentylidene (**I**) is formed.

These silica-bound Cr^{IV} dineopentyl and Cr^{IV} neopentylidene species have been characterized by GC/MS, IR, magnetic susceptibility, chemical reactivity, isotopic studies, and most notably by a kinetic study of the thermolysis reaction.

Although the silica-bound Cr^{IV} dineopentyl species is inert towards most gases, the silica-bound Cr^{IV} neopentylidene species catalyzes the polymerization of ethylene, propylene, and styrene.

Sublimation of $ZrNp_4$ onto a pyrogenic silica previously dehydrated at 500°C forms a product that consists of discrete Zr^{IV} tris(neopentyl) units bound to the silica surface. When H_2 is added to this product, a silica-bound Zr^{IV} monohydride (**II**) is formed along with methane, ethane, propane, and isobutene as the gas phase products.

The silica-bound Zr^{IV} trisneopentyl and Zr^{IV} monohydride species have been characterized by GC/MS, IR, EXAFS, elemental analysis, chemical reactivity, and isotopic studies.

The silica-bound Zr^{IV} hydride species displays some remarkable catalytic properties. For example, it catalyzes polymerization of alkenes such as ethylene and propylene. It also catalyzes the hydrogenolysis of alkanes under relatively mild conditions. Passage of neopentane and hydrogen over the catalyst results initially in the formation of isobutene, propane, ethane and methane; with time, ethane and methane are the sole gas phase products. A proposed mechanism for the hydrogenolysis reaction is given in Fig 1. When the catalyst is treated with light ($<C_{50}$) low-density polyethylene or polypropylene and hydrogen at 100°C, the polymer undergoes the hydrodepolymerization into lighter alkanes and eventually into ethane and methane.

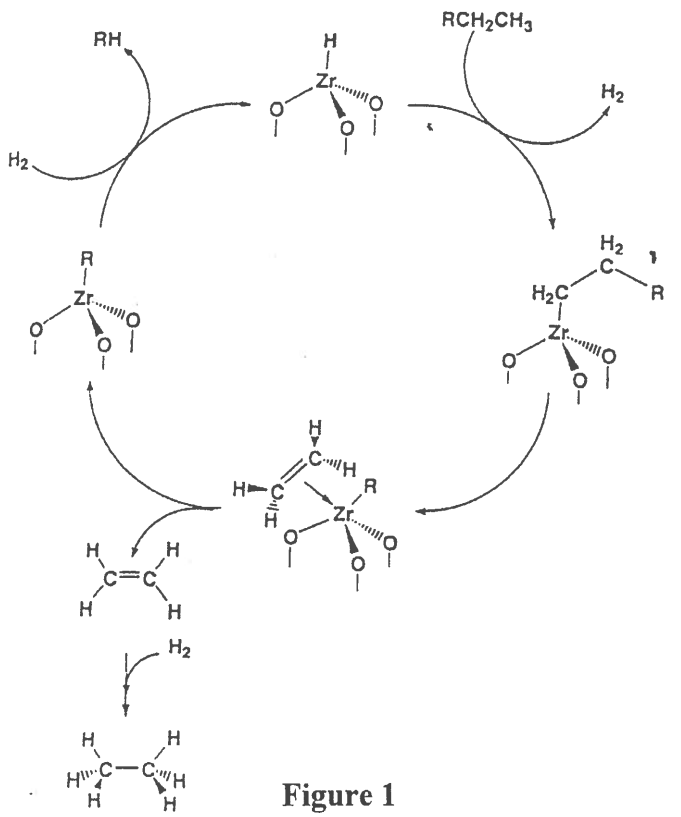

Figure 1

Sublimation of $TaNp_3$(neopentylidene) onto a pyrogenic silica previously dehydrated at 500°C forms a product that consists of a 65/35 mixture of Ta^{V}(neopentyl)$_2$(neopentylidene) and Ta^{V}(neopentyl)(neopentylidene) units bound to the silica. When H_2 is added to this product, discrete silica-bound Ta^{III} monohydride units (**III**) are formed.

The silica-bound Ta^{V} (neopentyl)$_2$(neopentylidene) and Ta^{V}(neopentyl)-(neopentylidene) species and the silica-bound Ta^{III} hydride species have been characterized by GC/MS, elemental analysis, IR, chemical reactivity and isotopic labeling studies.

This silica-bound Ta^{III} monohydride catalyzes the "metathesis" of linear or branched alkanes into the next higher and lower homologues at moderate temperature (25°C to 200°C). For example, ethane is transformed at room temperature into propane and methane. In addition, the ethane molecules mutually exchange a methyl group with one another, as is evidenced by isotope labeling experiments.

In conclusion, all three of these systems offer insight into the structure and reactivity of surface bound organometallic catalysts. In addition to this, the zirconium(IV) hydride system demonstrates promise towards the goal of developing polymer degradation catalysts and the tantalum (III) hydride system catalyzes the unprecedented process of alkane "metathesis."

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