Immobilized and Adsorbed Catalysts on Silica Surfaces: New Insights by Solid-State NMR Spectroscopy

Prof. Dr. Janet Bluemel, Department of Chemistry, Texas A&M University

February 3rd, 2022

Catalysis is immensely important in industry and academia. Two different directions in the quest for superior catalysts will be presented: (**1**) Catalysts immobilized on mesoporous oxide supports by chelating phosphine linkers[1-3] and (**2**) metallocenes adsorbed on silica[4,5] and other relevant surfaces.[6] Solid-state NMR spectroscopy is a powerful method to study these materials and different techniques will be presented.

(**1**) Wilkinson-type rhodium catalysts (e.g., Fig. 1) have been immobilized covalently via tripodal phosphine linkers with different alkyl chain lengths.[1] They have been characterized by HRMAS (High Resolution Magic Angle Spinning) techniques. Tripodal ligands inhibit the formation of nanoparticles and shield the metal centers from neighboring complexes and the reactive surface, and catalysts with unprecedented lifetimes have been obtained.[1]

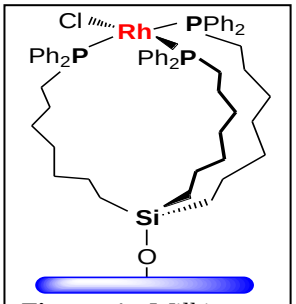

Figure 1. Wilkinson-type Rh catalyst immobilized on silica.[1]

Tripodal linker systems can also successfully be employed for other mononuclear and heterobimetallic catalyst systems,[2] including the Pd/Cu Sonogashira catalyst.[3] HRMAS allows the quantification of dynamic effects.

Figure 2. Pristine silica gel specimens (1), after adsorbing Cp_2Fe (2), and partially (3), and fully (4) oxidizing it to ferrocenium ions.[5]

(**2**) Metallocenes such as ferrocene (Cp_2Fe) and nickelocene (Cp_2Ni), a SAC precursor, can be adsorbed on high surface area materials[4-6] including silica (Fig. 2),[5] carbon nanotubes (Fig. 3) and activated carbon (Fig. 4).[6] The adsorption progresses quickly on favorable supports, even without a solvent. The underlying translational mobilities can be visualized, monitored, and quantified on a macroscopic scale when solid substrates migrate into the pores of large silica gel specimens (Fig. 2).[5]

The mobilities of the metallocene molecules on a surface lead to interesting solid-state NMR phenomena.[4-6] The isotropic spiraling movement across the curved walls of the support surfaces (Fig. 3) eliminate line-broadening anisotropic interactions in the solid state. For example, quadrupolar effects in ^2H solid-state NMR spectra (Fig. 4) vanish, and a narrow line is obtained for the adsorbed species.

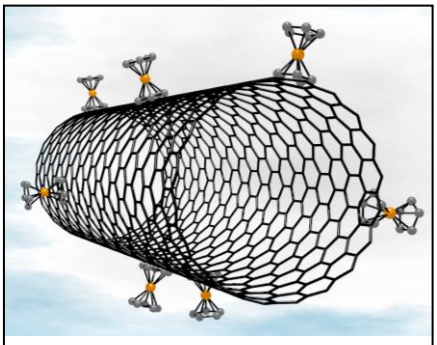

Figure 3. Artist's rendition of Cp_2Fe adsorbed on a carbon nanotube.

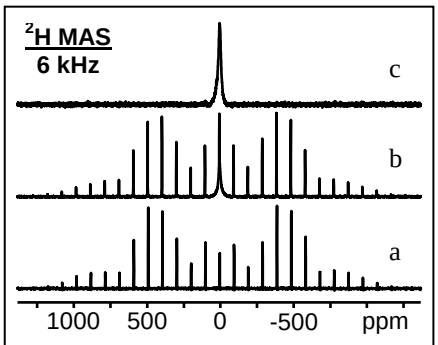

Figure 4. ^2H MAS spectra of Cp_2Fe-d_2. Polycrystalline (a), partially (b), and completely (c) adsorbed.[6]

Importantly, all metallocenes form well-defined monolayers on the surface. Their reduction with hydrogen leads to single atom catalysts.

---

(1) J. Guenther, J. Reibenspies, J. Blümel, *Mol. Catal*. **2019**, *479*, 110629. **(2)** K. J. Cluff, N. Bhuvanesh, J. Blümel, *Chem. Eur. J*. **2015**, *21*, 10138-10148. **(3)** J. C. Pope, T. Posset, N. Bhuvanesh, J. Blümel, *Organometallics* **2014**, *33*, 6750-6753. **(4)** P. J. Hubbard, J. W. Benzie, V. I. Bakhmutov, J. Blümel, *Organometallics* **2020**, *39*, 1080-1091. **(5)** K. J. Cluff, J. Blümel, *Chem. Eur. J.* **2016**, *22*, 16562-16575. **(6)** K. J. Cluff, J. Blümel, *Organometallics* **2016**, *35*, 3939-3948.