CHARACTERIZATION OF REACTIVE SITES IN SUPPORTED CATALYSTS BY $^{51}$V/$^{15}$N ROTATIONAL ECHO DOUBLE RESONANCE NMR SPECTROSCOPY: FORMATION OF PHENYLIMIDO GROUPS AT SURFACE-BOUND OXOVANADIUM SITES

C. Brown, R. Achey (FSU, Chemistry and Biochemistry); R. Fu (NHMFL); T. Gedris (FSU, Chemistry and Biochemistry); A.E. Stiegman (FSU, Chemistry and Biochemistry)

Introduction

Surface-supported transition metals containing multiply bonded ligand systems such as alkylidene and imido groups have long been proposed as key intermediates in heterogeneous catalytic reactions such as olefin metathesis, polymerization and ammoxidation. In spite of the importance of these proposed species, their positive characterization on catalyst surfaces has been difficult due to their low concentration and transient nature. We report here the generation of metal-imido functional groups at discrete silica-supported vanadium-oxo sites under catalytic conditions. Specifically, vanadium-oxo groups in a silica xerogel matrix react cleanly and quantitatively with aniline in a gas-solid reaction to generate a phenylimido group at the vanadium center with concomitant elimination of water.

Experimental

Characterization of metal-imido bond formation was carried out using $^{51}$V/$^{15}$N rotational echo double resonance (REDOR) NMR spectroscopy where the more sensitive quadrupolar $^{51}$V nucleus was monitored while the $^{15}$N nucleus was pulsed. While REDOR has been used to characterize a number of dense and porous inorganic solids and both one- and two-dimensional solid-state NMR has been used to characterize surface-grafted organometallic species, we believe this is the first use of REDOR to elucidate such sites.

Results and Discussion

Vanadium oxide supported on silica was fabricated using an established sol-gel derived procedure. Exposure of a monolithic 0.25 mol % V-silica xerogel to vapor phase aniline in a dry nitrogen flow showed systematic changes in the UV-Vis spectrum begin to occur between 120-175 °C with clean conversion to a distinct product observed.

Rotational echo double resonance spectroscopy (REDOR) was used to establish the presence of direct covalent bonding between the V and the N. Because of the low concentration of sites present on the surface, the REDOR fraction was measured by monitoring the more intense $^{51}$V NMR signal, while applying two $\pi$ pulses per rotor period to $^{15}$N using the pulse sequence shown in Figure 3a. The $^{51}$V echo was measured with and without the $^{15}$N pulses and the REDOR fraction, $DS/S_0$, plotted as a function of rotor evolution. Consistent with a short covalent bond length, after 3 msec of dephasing 60 % of the signal is lost. The best fit of the data was with a dipolar coupling constant of 419 Hz. In small molecule analogs vanadium(V)-nitrogen covalent lengths typically range from around 1.60-1.70 Å for arylimido groups and 1.9-2.0 Å for amido groups. Consistent with these covalent lengths the V-N bond length obtained from the fit was 1.96(±0.09) Å. While this is longer than expected for an imide, it has been established that bond length estimates determined from fits to the REDOR experiment tend to be longer than the experimental distances found through x-ray crystallography. This has been attributed to molecular motion and thermal dynamics that may partially average the dipolar couplings between two spins.

Conclusions

Discrete catalytic sites containing metal-ligand multiple bonds have been generated on a silica surface. Specifically, vanadium-imido functional groups were generated by a gas-solid reaction.

Acknowledgements

Funding was provided by the Air Force Office of Scientific Research through MURI 1606U8.