

Characterisation of Rhodium and Iridium Hybrid Catalysts by X-ray Absorption Spectroscopy

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Transition-metal catalysis is ubiquitous in synthetic chemistry and among the most important processes in the chemical industry. Surface immobilised transition metal catalysts, known as hybrid catalysts, combine the efficiency of heterogeneous- and the selectivity of homogeneous catalysts. Advantages of hybrid catalysts over traditional homogeneous analogues are stability and simplified removal of the catalyst from the reaction mixture, which provides access to urgently needed more efficient and greener processes.¹ Here, we present a series of new hybrid rhodium- and iridium based pyrazole-triazole (PyT) complexes attached to carbon black (CB) with varying tether lengths. The synthesis of the long alkyl chain ligands was accomplished through tin mediated acylation of aromatic systems² and Click-chemistry, giving the PyT-group. This was followed by metal coordination, affording the Rh- and Ir-complexes. The catalysts are anchored to the surface via a phenyl group, which is connected to an alkyl linker of varying lengths bearing the catalytically active metal complex as head group. We immobilised the catalysts on CB using radical methodology. Initially, we optimised grafting conditions to gain control over the metal loading on the surface. Furthermore, we attached both rhodium- and iridium catalysts simultaneously to obtain heterobimetallic mixed layers.³ The developed hybrid catalysts were analysed using a number of techniques, including SEM/EDX, XPS.

The hybrid catalysts were all found to be efficient catalysts that were robust and recyclable. In particular, they promote the hydrosilylation of phenylacetylene, generating a mixture of the $\beta(E)$,- $\beta(Z)$ and α and isomers of the respective silylated alkenes. Interestingly, the homogeneous Rh complexes give a mixture of all isomers, while the same Rh complexes immobilised on CB are selective for the α -isomer. In contrast, both the homogeneous and hybrid Ir complexes give the $\beta(Z)$ -isomer. XAS measurements were performed at the Australian Synchrotron to probe possible surface effects influencing the catalytic activity of the hybrid catalysts. We recorded EXAFS spectra of the monometallic and heterobimetallic hybrid complexes at the Rh K- and Ir L3-edges, respectively, providing an additional tool for probing surface effects in catalysis.

References

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No

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