Design of organometallic complexes as precursors for catalysts with tuneable properties

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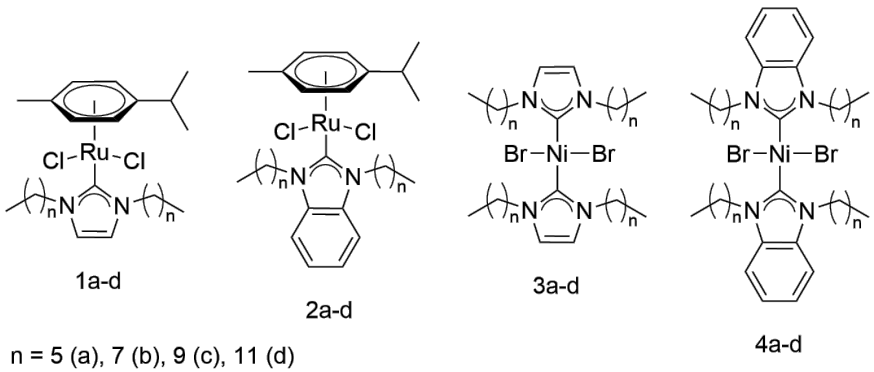
Coreshell nanoparticles (CSNPs) show excellent stability and selectivity for catalysis due to the presence of a protective shell encapsulating the active nanoparticle surface.[1] The increased stability and selectivity have proven beneficial for biomass conversion to value-added chemicals[2] – an important topic for a more sustainable future. However, there are major challenges with reproducibility and control over nanoparticle properties, particularly in the field of heterogeneous catalysis.[3] Herein we propose a strategy for the reproducible synthesis of nanoparticles with adjustable properties to help bridge the gap between catalyst preparation and catalyst properties. By correlating the nature of the organometallic precursors and CSNP preparation method parameters with the structure of the resulting CSNPs, we are developing a methodology for preparing CSNPs with tuneable physical properties. Studying the relationship between CSNP physical and chemical properties allows us to identify key features that indicate greater stability and higher activity in C-O bond hydrogenolysis.

A variety of ruthenium and nickel complexes featuring *N*-heterocyclic carbene (NHC) ligands (Ru-NHC and Ni-NHC) were prepared and used to generate NPs. NHC ligands featuring alkyl side chains (Fig. 1) were chosen to emulate the carbon chains of many surfactants previously used to generate stabilized NPs.[4] The length of the carbon chain was varied to study the effect on shell thickness and porosity, and, as a result, the activity, selectivity, and stability of the NPs. After a sequential chemical reduction and pyrolysis of the organometallic precursors, the physical properties, such as shell thickness, can be related to the precursor nature and variables in the NP synthesis method. After application to the C-O bond hydrogenolysis of lignin model compounds (diphenyl ether, benzylphenyl ether, and phenethyl phenyl ether) under mild conditions (140 °C and 15 bar H_2), structure-activity relationships identify the most important physical properties for predicting catalytic activity, stability, and selectivity.



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