The development of well-defined model catalysts whose catalytic properties can be assessed in a rational manner is of great importance to fundamental studies of catalysis, and vital to the development of new catalysts. The focus of this thesis was to design heterogeneous ruthenium (Ru)-based catalysts with well-defined structures, and to identify the correlation between their structures and catalytic performance for the liquid phase hydrogenation of bio-derived organic acids and aldehydes.

We evaluated colloidal-based routes for the preparation and activation of supported Ru nanocatalysts. In comparison to thermal decomposition with thioether as stabilizer or phase-transfer synthesis with amine as stabilizer, polyol reduction with polymers as stabilizer gave the best results for synthesizing monodisperse colloidal Ru NPs in high yield in a moderate reaction time over a broad range of reaction temperatures. Sonication-assisted colloidal deposition was more efficient than direct colloidal deposition for anchoring the Ru NPs on ordered mesoporous silica (MSU-F) support. Activation of the supported Ru NPs to remove the organic stabilizer used in the synthesis was explored using three thermal treatments: gentle oxidation at 150°C, thermal reduction at 350°C, and Argon-protected calcination at 650°C. After treatment, the solid catalysts were characterized by several physical and chemical methods and their reactivity was assessed by the aqueous phase hydrogenation of pyruvic acid to lactic acid as a model reaction. The conclusion from these studies was that argon-protected calcination is the most efficient procedure for activating the MSU-F-supported Ru nanocatalysts.

We then investigated the effect of particle size on the catalytic activity and selectivity of the supported Ru NPs, using the liquid phase hydrogenation of cinnamaldehyde (CAL) as the model reaction. Colloidal Ru NPs of different size groups were synthesized by adjusting the polyol reduction parameters. It was observed that the formation of Ru NPs can occur under either thermodynamic or kinetic control, with the final size of the NPs determined by a balance between the two pathways. After sonication-assisted deposition of the size-tuned Ru NPs on MSU-F and
subsequent Ar-protected calcination, we observed well-dispersed Ru NPs on the support with no signs of agglomeration and no damage to the ordered structure of the support. The uniformity and crystallinity of the supported Ru NPs in each catalyst were also improved, likely due to sintering and annealing effects during thermal activation. The primary product of CAL hydrogenation over all the supported Ru NPs was cinnamyl alcohol (COL), and varying the size of the NPs did not affect this selectivity. We observed a non-linear relationship between the size of Ru NPs and their subsequent activities, which is an indication that not all the surface atoms of the NPs were active sites. The size of the Ru NPs also has a marked effect on the apparent activation energy.

Finally, we correlated the compositions of the Ru-based bimetallic catalysts to their selectivity and catalytic activity for CAL hydrogenation. The colloidal Ru-Pd bimetallic NPs as well as their monometallic counterparts were synthesized by polyol co-reduction of the metal precursors, impregnated into MSU-F support via sonication-assisted deposition, and activated through Ar-protected calcination. The supported NPs in each catalyst complex were well dispersed on MSU-F, as uniform spheres with sizes ranging from 10 to 12 nm. We also noted that the supported bimetallic NPs exhibited an alloyed crystal structure, with uniform distribution of the two metals. The hydrogenation of CAL over all the supported Ru-Pd bimetallic NPs and the monometallic Pd NPs produced either hydrocinnamaldehyde (HCAL) or hydrocinnamyl alcohol (HCOL) as the major product, with the mole ratio of HCAL to HCOL strongly dependent on the metal composition of the catalysts. The supported bimetallic NPs exhibited higher turnover frequencies (TOF) than the monometallic Ru NPs, with the enhancement proportional to the Pd fraction up to 50 mol%, presumably due to synergetic effects. Similarly, we observed that the apparent activation energy is strongly dependent on the metal composition of the supported NPs.

In summary, this research has provided new routes for the rational design of Ru-based heterogeneous catalysts with well-defined structures, and new insights into the relationship between structure and catalytic performance of Ru-based catalysts in multiphase hydrogenation of bio-based organic acids and aldehydes.

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