

Earth-Abundant Transition Metals in Catalysis (Draft)

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Metal-catalyzed asymmetric homogeneous hydrogenation is likely the most established enantioselective process in chemical industry. Since the 1960's, the efficient hydrogenation of C=C, C=O and C=N bonds has been centered on precious transition metals (i.e. Rhodium, Ruthenium, Iridium). Over the last 30 years the chemical industry additionally encompassed metal-catalyzed C–C and C–N-cross-coupling reactions, mainly relying on catalytic amounts of precious Palladium (Pd). The cross-coupling approach allows to quickly synthesizing products with high complexity from readily available building blocks and therefore higher catalyst-loadings were tolerable. In recent years, high price-pressure on these rare transition metals triggered the development of novel reactions that are catalyzed by earth-abundant metals such as Manganese, Cobalt, Nickel, Copper and even iron.

Apart from the cost advantage and a usually more attractive toxicology profile, the low-priced first-row transition metals were found to have a distinct reactivity profile compared to the 'classic' precious metals. For example, Manganese base catalyst allow the efficient catalytic reduction of ester functionalities, a process that often still relies on the use of stoichiometric amounts of reactive inorganic hydrides. In the meantime, Cobalt appears to be capable of substituting expensive Rhodium in the asymmetric hydrogenation of e.g. enamines or enamides. Nickel's unique properties enable *inter alia* stereoselective C(sp²)-C(sp³)-bond formation as well as the development of cross-electrophile couplings. Copper is back in the spotlight and in combination with novel ligands C-N-couplings are achievable under mild conditions and with economic catalyst loadings. Additionally, the metals Nickel and Copper enable the catalytic stereoselective hydro-functionalization to give chiral amines or other enantioenriched building blocks of high value in only one step from alkenes, which can be regarded as the prime example of feedstock chemicals.