Hydrodeoxygenation (HDO) of phenol over nickel nano-particles of different size (5-22 nm) supported on SiO₂ has been investigated in a batch reactor at 275 °C and 100 bar. Deoxygenation was only observed as a consecutive step of initial hydrogenation of phenol at the given conditions. Both the hydrogenation and deoxygenation reaction were found to be Ni-particle size dependent. Rapid hydrogenation of phenol to cyclohexanol was achieved over the catalysts with large particles, while the rate of deoxygenation of cyclohexanol was slow. For the catalysts with small Ni particles, the opposite behavior was observed. Specifically, the turn over frequency (TOF) of hydrogenation was 85 times slower for 5 nm particles than for 22 nm particles. On the contrary, the TOF of cyclohexanol deoxygenation increased by a factor of 20 when decreasing the particle size from 20 nm to 5 nm. A simple kinetic model showed that the rate limiting step for phenol HDO shifted from deoxygenation to hydrogenation when the particle size was below 9-10 nm. Surface site population theory evidenced that the deoxygenation reactions were favored on step/corner sites, giving higher deoxygenation rates at small particles. For hydrogenation, the influence of particle size on the rate could be related to the size of the Ni facets with larger facets thus being better.