Nanoparticles of iron and nickel are promising candidates as nanosized soft magnetic materials and as catalysts for carbon nanotube synthesis and CO methanation, among others. To understand geometry- and size-dependent properties of these nanoparticles, phase diagram of Fe/Ni alloy nanoparticles was calculated by density functional theory and cluster expansion method. Ground state convex is presented for FCC, BCC, and icosahedral particles. Previous experimental observations were explained by using multiscale model for particles with realistic size (diameter ≥ 2 nm). At size 1.5 nm, geometry changes from BCC at low X(Ni) to icosahedral at high X(Ni). FCC is stabilized over icosahedral geometry by increasing number of atoms from 561 to 923. In large FCC particles, there is enrichment of Fe atoms from core to shell beneath surface, while surface and core are enriched by Ni atoms. Catalytic enhancement effect in CO methanation was found to be due to Ni incorporating in the active sites which brings adsorption energy of oxygen closer to the optimum. The predicted phase diagrams and implications on catalysis are expected to help rationalisation of experimental results and provide guidance for design of Fe/Ni-based nanomaterials.