Pt based nanoparticles are crucial in many areas of modern life, and particularly in catalytic applications such as automotive diesel exhaust or fuel cells [1]. Solvothermal synthesis methods, i.e. solution based synthesis under high pressure and high temperature conditions, have been developed as one of the premier methods to obtain Pt based nanoparticle catalysts due to the excellent control of nanoparticle characteristics such as size, crystallinity and morphology, which all strongly affect the catalytic performance. However, insight into the reaction mechanism leading to nanoparticle formation under solvothermal conditions is lacking due to the experimental difficulty in obtaining atomistic information on the nanoscale – this is in general called “the nanostructure problem” [2]. Using in situ total X-ray scattering in combination with powder X-ray diffraction and pair distribution function analysis we unravel the formation mechanism of Pt and PtPb nanoparticles under supercritical ethanol conditions. The metal complex structures of two different platinum precursor solutions, chloroplatinic acid and Pt(acac)\(_2\) (acac = acetylacetonate) provide atomic-scale detail about the nucleation mechanisms. In case of chloroplatinic acid, an octahedral PtCl\(_6\)\(^{2-}\) precursor complex is reduced in two steps to form Pt nanoparticles [3]. Whereas, in case of Ptacac, a square planer Ptacac complex exist in solution which get reduced to form Pt nanoparticles. The stronger Pt-O chemical bonding in the Pt(acac)\(_2\) precursor complex compared with the Pt-Cl bonding in the chloroplatinic acid leads to a much slower reduction of the Pt center in case of Ptacac. This allows more favorable co-reduction conditions providing a pathway for formation of phase-pure intermetallic PtPb. The similar reduction rate of both Pt(acac)\(_2\) and Pb(acac)\(_2\) precursors allow development of a facile continuous flow supercritical ethanol process for obtaining phase-pure hexagonal PtPb nanocrystals. The study thus highlights the importance of in situ studies in revealing atomic-scale information about nucleation mechanisms, which can be used in design of specific synthesis pathways, and the new continuous flow process to obtain PtPb nanocrystals holds potential for large scale production.


Keywords: Total X-ray scattering, Reaction mechanism, Nanoparticles