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Supercritical Flow Synthesis of $\text{Pt}_{1-x}\text{Ru}_x$ Nanoparticles:

Comparative Phase Diagram Study of Nanostructure versus Bulk

Martin Bondesgaard,¹ Aref Mamakhel,¹ Jacob Becker,¹ Hidetaka Kasai,^{1, 2} Gilles Philippot,³ Martin Bremholm¹ and Bo B. Iversen^{1*}

¹Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, DK-8000 Aarhus, Denmark

²Faculty of Pure and Applied Sciences, TIMS and CiRfSE, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

³CNRS, Universite Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

* Email: bo@chem.au.dk

Abstract

The thermodynamic stability of nanocrystals is different from bulk systems, and nanoscale phase diagrams are to a large degree unknown. Here we present a systematic investigation of the $\text{Pt}_{1-x}\text{Ru}_x$ phase diagram through supercritical flow-synthesis of $\text{Pt}_{1-x}\text{Ru}_x$ nanoparticles across the entire compositional range. The synthesis was done in stoichiometric steps of 0.1 using an ethanol-toluene mixture as solvent at 450°C and 200 bar. The products were characterized by high resolution synchrotron powder X-ray diffraction, transmission electron microscopy and elemental mapping of individual particles using energy-dispersive X-ray spectroscopy. The diffraction data revealed a single phase fcc alloy for $x \leq 0.2$, while an additional hcp phase emerges as x approaches 1. This behavior deviates significantly from the bulk phase diagram where a biphasic region is only observed

for $0.62 < x < 0.8$. Thus, compositional design of Pt-Ru alloys is more flexible on the nanoscale opening up significant possibilities for catalyst optimization. Rietveld refinements and microstructural line profile analysis show that the fcc unit cell dimensions follow Vegard's law within a good approximation. On the other hand, crystallite size, microstrain, phase content and hcp c/a ratio depend non-linearly on x but shows some correlation to the bulk phase diagram. Elemental mapping show the nanoparticles to be homogeneous, but in some cases fcc-hcp phase boundaries and modulations in the elemental distribution were observed. All samples below $x < 0.3$ exhibit a spherical morphology. At higher ruthenium content, $x \geq 0.3$, another morphology emerges with elongated particles together with the dominating spherical morphology. The TEM average particle sizes ranging from 5.0(8) to 10.4(7) nm.

Introduction

Recent decades have shown growing demands for noble metals in a variety of applications such as catalysis, electronics, optical sensing, and photothermal therapy.¹ Among these are platinum (Pt), which has exhibited increasing costs with consequent incentives for reducing consumption e.g. through design of effective, durable yet Pt-deficient catalysts.¹ To this end, an obvious mean is the use of nanoparticles. Several factors affect the performance of a catalyst including particle size (surface area), crystallinity, morphology, crystal structure, degree of agglomeration, surface chemistry and elemental composition by alloying or atomic substitution. Great efforts have been put into gaining control of these parameters in order to optimize catalyst performance.^{2, 3} In this regard, alloying Pt with cheaper elements has the explicit advantage of further decreasing raw material costs. Among alloys the Pt-Ru system has attracted attention due to excellent catalytic properties⁴⁻⁷ for many applications, e.g. as catalysts in fuel cells.^{4, 8} Here, the overall driving factor is

not only the inclusion of comparatively cheap Ru,¹ but also its ability to greatly diminish the detrimental effect of Pt being poisoned by CO.⁹

A wide variety of controlled methods to synthesize nanoparticles have been developed, and the literature on Pt-systems is large and ever expanding. Among the typical methods for preparing Pt-based catalysts are solvothermal,^{10, 11} polyol reduction,¹² chemical vapor deposition,^{13, 14} wet impregnation,^{15, 16} aqueous solution with different reducing agents (NaBH₄, hydrazine etc.),⁶ flame aerosol,¹⁷ electromagnetic radiation assisted reduction^{18, 19} etc. More than 20 years ago Adschiri and coworkers developed a method to synthesize nanoparticles in supercritical fluids (SCFs).²⁰ They have a range of unique properties, e.g. gas-like transport properties combined with liquid-like solvation capability and density, which can be effectively manipulated by changes in pressure and temperature. This makes SCFs very useful as a synthesis medium for nanoparticles. Indeed, a wide range of complex nanomaterials have been prepared during the past decades.²⁰⁻³⁰

In the case of the Pt_{1-x}Ru_x system, most of the previous solvothermal synthesis studies were done for the pure metal or for a limited number of alloy compositions. In the majority of studies, various types of batch syntheses were used.^{5, 8, 31-34} Two studies report on solvothermal flow-synthesis of Pt, PtRu and Ru at different temperatures. Mi *et al.* reports the formation and growth mechanism of PtRu nanoparticles.³⁵ Most continuous solvothermal studies are for pure Pt-nanoparticles,^{10, 26, 36, 37} again including Mi *et al.* employing pulsed-flow supplemented by *in-situ* studies of the formation and growth of Pt. Mi *et al.* also reported on the formation of pure Ru nanoparticles³⁷ using pulsed flow synthesis and including details on their formation and growth mechanism based on different precursor materials. To the best of our knowledge, only two other continuous-flow synthesis methods have been reported for this system, continuous flame aerosol synthesis¹⁷ and a continuous thermal CO-reduction method.³⁸

Pt_{1-x}Ru_x nanoparticles have been reported to exhibit interesting phase behavior that deviates from the bulk phase diagram.^{35, 37} The hcp phase is the thermodynamically stable phase while fcc is metastable.³⁷ Recently, synthesis of phase pure fcc Ru was reported.^{37, 39} Here, we present the first systematic investigation of flow-synthesized Pt_{1-x}Ru_x nanoparticles across the entire compositional range and investigate the particle sizes, microstructures, morphologies and allotropism.

Experimental section

Materials

The solvents toluene (99.9%) and absolute ethanol were purchased from Sigma-Aldrich and VWR respectively. The metal precursors Pt(acac)₂ (acac = acetylacetonate, 98%) and Ru(acac)₃ (≥97%) were purchased from Strem Chemicals and Sigma-Aldrich, respectively. All chemicals were used as received.

Synthesis

The syntheses were carried out in a flow-reactor shown schematically in **Figure 1**.^{40, 41} The metal precursors were dissolved in an 82:18 vol% mixture of ethanol-toluene. The metal concentration was 10 mM. A total of 11 syntheses were carried out with composition increments of 10 mol% from Pt_{0.0}Ru_{1.0} to Pt_{1.0}Ru_{0.0}. A 200 mL precursor solution was loaded into an injector vessel⁴² in order to prolong the lifespan of the pumps. The flow-rates of precursor and solvent (absolute ethanol) were 7 mL/min and 15.6 mL/min, respectively. The pressure was controlled by a proportional relief-valve (PRV) set to 200 bar. The solvent stream was preheated to 450°C and subsequently mixed with the ambient temperature precursor stream in a T-piece mixing geometry. The mixed stream passed through a vertical reactor also heated to 450°C, and the residence time in the reactor falls in the range 6-11 s as calculated from reactor volume, flow-rate and fluid density obtained at either $T_{\max}$

(450°C) or T_{mixing} (318°C), respectively. Here, the solvent density⁴³ is assumed equal to that of pure ethanol. The product stream was cooled to ambient temperature before collection of the products. The collected product suspensions were centrifuged and washed with ethanol several times and finally dried at ambient conditions.

Figure 1. Diagram showing the reactor used for continuous flow supercritical synthesis of $\text{Pt}_{1-x}\text{Ru}_x$ nanoparticles.

Characterization

High resolution synchrotron powder X-ray diffraction (S-PXRD) measurements were performed at beamline BL44B2⁴⁴, SPring-8, Japan, using a wavelength of 0.50037 Å. The data were analyzed with the FullProf software suite⁴⁵ using both Rietveld and Le Bail refinements. The instrumental profile broadening was estimated by refinement of a model to data collected on a CeO_2 standard sample (NIST SRM 674b) and included in the refinements (IRF file). The background was described by a 12th order polynomial. Peak profiles for the phase region $x < 0.3$ were modeled with the Thompson-Cox-Hastings pseudo-Voigt function; for $x \geq 0.3$ when the second phase emerges, a Le Bail model was used. Trial refinements showed that a purely Lorentzian line profile (X and Y parameters) was

adequate, since the Gaussian parameters refined to values of zero (within one standard deviation) when the instrumental profile broadening was included. The X and Y profile parameters are related to the crystallite strain and size, respectively. The crystallite size was determined using the Scherrer equation. The Rietveld refinements were also used to quantify the weight fraction of the observed phases. Transmission Electron Microscopy (TEM) was performed on a Philips CM20 instrument equipped with a LaB₆ filament operated at 200 keV. High resolution (HR) TEM images and elemental mapping by energy-dispersive X-ray spectroscopy (EDX) measurements were carried out on a FEI "Talos" F200X analytical (S)TEM-microscope operated at 200 keV. The program ImageJ (FIJI) was used for statistical size-analysis of the nanoparticles and for the determination of *d*-spacing from HR-TEM images by Fast Fourier Transformation (FFT) of individual domains showing well-defined lattice fringes.

Results and discussion

Phase behavior

The measured synchrotron PXRD patterns are shown in **Figure 2a**. For $x \leq 0.2$ a single fcc phase is observed, while for $x \geq 0.3$ reflections indexed to the hcp phase become increasingly dominant. This is in contrast to the bulk phase diagram⁴⁶ wherein a single-phase fcc alloy exists for $0 < x < 0.62$ and an hcp alloy for $0.8 < x < 1$. In the intermediate range ($0.62 < x < 0.8$) a biphasic region exists. The PXRD data obtained in this study show a significant expansion of the biphasic region when moving from bulk to nanoparticles. The region of single phase hcp is completely eliminated, leaving only one monophasic region in the whole phase diagram (fcc at $x \leq 0.2$). Similar behavior has been reported by Kusada *et al.*⁴⁷ on the Pd_{1-x}Ru_x system where a large biphasic region was found consisting of the fcc and hcp phases.

Figure 2. a) S-PXRD for the $\text{Pt}_{1-x}\text{Ru}_x$ system with Bragg reflections for the fcc phase (diamonds) and the hcp phase (solid circles). b) Magnified 2θ -window to clarify peak shifts.

Phase fractions were derived from Rietveld refinements in the biphasic region^{48, 49} and they are plotted against the composition in **Figure 3a**. The fraction of the hexagonal phase gradually increases with growing ruthenium content. A small discrepancy to this trend is seen in the step from $x = 0.9$ to $x = 1.0$, which may arise from the absence of Pt in the last sample. The growing hcp content is consistent with a transition towards the stoichiometric range where the hcp phase is thermodynamically favored.

The crystal strains extracted from the Rietveld refinements for both the fcc and hcp phases are plotted in the lower part of **Figure 3a**. The fcc phase shows an increasing strain from $x = 0.0$ to 0.4, where it becomes roughly constant from 0.4 to 0.6. This reflects the stress imposed on the fcc structure by the hcp-favoring ruthenium. From $x = 0.6$ to 0.8 the fcc strain abruptly decreases which correlates well with the phase segregation seen in the bulk phase diagram.⁴⁶ Generally, from $x \geq 0.5$ the hcp phase exhibits the least strain of the two phases, a reflection of its thermodynamic stability

in elemental bulk Ru and the driver of its growing volume fraction. Meanwhile, at $x \geq 0.8$ the strain in the receding fcc phase once more increases as now imposed by the dominant hcp phase.

Figure 2b shows the progressive peak shift toward higher scattering angle with increasing Ru content, confirming the existence of a solid solution. Unit cell parameters were extracted from the Rietveld refinements, and in **Figure 3b** these are plotted against composition for the fcc as well as the hcp phase. For fcc, the a -axis of the unit cell follows a decreasing, linear trend with increasing Ru content. This is in agreement with Vegard's law. Kusada *et al.*⁴⁷ reported a similar trend for the $\text{Pd}_{1-x}\text{Ru}_x$ system where it was shown possible to alloy the two elements over the entire composition range. The same trend is reflected in the c -axis in the hcp phase, whereas the a -axis remains nearly constant. These data are plotted as $a \cdot 1.633$ (the c/a ratio of an ideal hcp structure) in order to clarify deviations from ideal behavior e.g. compression or expansion. The a -values for hcp are given in the supporting information table S.1.

Figure 3. a) Weight fractions in the two phase region and (below) strain values for the two phases obtained from the Rietveld refinements. Dashed lines indicate the bulk phase diagram. b) Unit cell parameters extracted from Rietveld refinement. c) Volume per atom for the two phases. d) The c/a ratio for hcp and interatomic distances obtained from Rietveld refinement.

Figure 3c plots the volume per atom for the two phases. For a given composition, the fcc phase has a higher volume than the hcp phase which correlates with the trends in unit cell length and bonding distance for the two phases. It also reflects how the hcp phase offers a closer packing than the fcc solid solution, which in turn is related to the phase segregation into fcc and pure hcp and reflects the thermodynamic relationship between the two phases. To investigate the bonding nature in the two phases the interatomic distance $\langle M-M \rangle$ is plotted in **Figure 3d**. The $\langle M-M \rangle$ distance in fcc decreases smoothly as the Ru content increases. This behavior is expected from the metallic radii with that of Ru being smaller than Pt (134 and 139 pm, respectively⁵⁰). The same trend is observed along the *c*-direction in the hcp phase while no contraction is found in the *a,b*-plane. The fcc interatomic distance is found to be larger than distances along all axes in hcp for $x < 0.9$, which is seen as a “driver” of the hcp formation as it implies weaker bonding in the fcc structure compared with the hcp structure. The bond strength in hcp only shows significant changes in the *c*-direction. The compression can be illustrated from the *c/a* ratio, which starts from a value close to the ideal ratio (1.633) and then decreases toward close to the bulk ruthenium value at $x = 1.0$. This trend is in agreement with the observed trend in strain, which corroborates the transition from a metastable to a more thermodynamically favored state.

Nanoparticle sizes

The particle sizes observed in TEM and the crystallite sizes derived from PXRD are shown in **Figure 4**. Note that figures for TEM have been converted from being number weighted into volume weighted in order to offer direct comparison with PXRD ($\langle D \rangle_{\text{PXRD}} = \langle D^4 \rangle / \langle D^3 \rangle$). The coincidence between TEM and PXRD is striking. It is concluded that the nanoparticles are fully crystalline, as also

confirmed by HR-TEM (presented below). Considering, the volume weighting of the sizes, it is not surprising that size estimates from PXRD follow the crystal phase with the largest particles (revealed by TEM) at any given composition. Generally, stepping up from $x = 0$ the particle size gradually decreases from approx. 10 nm to 5 nm at $x = 0.5$. In the region $x = 0.4-0.6$ it levels out and becomes more or less constant at higher values of x . The trend of decreasing particle size for alloys compared to pure metals has been previously reported.³¹ A correlation was found by Ouyang *et al.*⁵¹ showing an increased strain with decreasing particle size. This could be a contributing factor to limit the particle growth in combination with additional effects discussed below.

Figure 4. Average particles size from TEM (volume weighted) and the crystallite size for the two phases (cubic and hexagonal) from PXRD. Dashed lines indicate the bulk phase diagram.

Another driving factor for the splitting into two phases can be found in the *in-situ* studies by Mi *et al.* The temperature-resolved study of pure Ru (200, 250, 300 and 400°C) identified a trend that the amount of fcc phase was declining as the temperature was increased.³⁷ The *in situ* PXRD data revealed that the phases form simultaneous. This is evidence that the presence of fcc Ru is kinetically driven and implies a lower energy barrier for formation of fcc compared to hcp Ru. In the

in situ PXRD study on Pt_{0.5}Ru_{0.5}¹¹ it was concluded that Pt nanoparticles are formed first followed by the formation of a surface layer of Ru on Pt nanoparticles which diffuse into the Pt nanoparticles to form the Pt_{0.5}Ru_{0.5} alloy. Unfortunately this measurement is made at 200°C, with no data existing for 400°C. In the present study, done at 450°C, the time scale of the syntheses is significantly shorter (6-11 seconds) than that observed for this diffusion process (2 min). Based on this, it appears that the high temperature allows completion of parallel reactions of Pt-Ru and pure Ru due to different reaction time for Pt and Ru formation. On the other hand the short reaction time means that diffusion cannot be completed leading to two distinct, separate phases crystallize even at low Ru contents. This is supported by STEM-EDS (**Figure 7a-d**) where some particles are found to have oblong areas with different structures and corresponding variation in composition ranging from Ru- and Pt-rich regions, respectively. More details on these particles are provided in section 3.3.

It is possible that the relationship between fcc and hcp is not explained by kinetics alone, i.e. they could be affected by thermodynamic factors as well. In particular, it is known that many metastable phases cannot exist above a certain critical particle size⁵²⁻⁵⁵ due to a lower surface energy than that of thermodynamically favored (bulk) phases. Hence, metastability occurs when the particle becomes sufficiently small. An example is the study by Kitakami *et al.*⁵³ on Co nanoparticles, where the otherwise metastable fcc phase was found to be stable (phase pure) under 20 nm while only the hcp phase was observed for sizes above 110 nm. For intermediate sizes, a mixture of the two phases was observed with a decreasing amount of the fcc phase as particle size increased. In the present study, the crystallite size of the hcp phase is persistently lower than that of the fcc phase up until $x \geq 0.9$. If it is assumed that the fcc phase is thermodynamically stable in the region $0 < x < 0.62$ (and the hcp phase metastable), this behavior could be correlated to the bulk phase diagram. For the nanoparticle phase diagram in the region $0.62 < x < 0.80$ both phases coexist; this would

correspond to the bulk phase in the region $0.8 < x < 1.0$. In the nanosystem, the above thermodynamical argument hinges on the assumption that the critical particle size “inverts” in the composition range $0.62 < x < 0.8$, rendering the fcc metastable for $x \geq 0.8$. However, literature provides no clear picture of why such an inversion would occur. The matter of a potential critical particle size in this nanostructured system, must therefore be a subject of further studies. Yet a proposed explanation for the presence of a maximal critical particle size can arise from a combination of the facts discussed previously. When formation of a metastable structure is controlled by kinetics, the temperature need to be kept under a certain threshold to form the structure of interest to avoid sufficient energy in the system to pass the larger energy barrier for the the thermodynamically favored structure. When the reaction temperature is kept below this threshold, there is often also insufficient energy to initiate the further particle growth by either Oswald ripening or coalescence. These conditions favor that the particles size remain small, and this also makes the surface energy more dominant term in determining phase stability (higher fraction of surface atoms). When particle formation takes place above the temperature threshold, then the balance between the conditions is shifted toward forming the thermodynamic favored phase either partly or fully as seen in the study by Mi *et al.*³⁷ This may explain why inversion of crystallite sizes is observed for the two phases.

Table 1 shows a comparison with reported values (at 400 °C) for crystallite size and unit cell parameters at $x = 0$ and 1.^{10, 37} For $x = 0$ at 400°C,¹⁰ the unit cell parameter found by Mi *et al.* are a bit below that presented here (450 °C), whereas the crystallite size obtained is significantly larger. For Ru nanoparticles ($x = 1$) the unit cell parameters for the hcp phase are reported to slightly exceed the present data.

Table 1. Crystallite size and unit cell parameters

	Mi <i>et al.</i> ^{10, 37}		This study	
	Crystallite size	Unit cell parameters	Crystallite size	Unit cell parameters
x = 0.0	24.7 nm	3.903 Å	10.3 nm	3.915 Å
x = 1.0	4.9/8.6 nm (fcc/hcp)	2.728/4.325 Å (a/c)	4.3/5.9 nm (fcc/hcp)	2.704/4.292 Å (a/c)

In the studies by Mi *et al.*,^{10, 11, 37} the precursor Ru(acac)₃ resulted in a mixture of fcc and hcp Ru at all temperatures (200-400°C) whereas for the RuCl₃, pure hcp phase was consistently observed. This suggests that the formation of hcp Ru nanoparticles presumably progresses through a reactions path mediated by anions. This corresponds well to literature where halide ions (e.g chloride) are known to be templating agents in the synthesis of metal nanoparticles e.g. to favor certain crystal structures^{37, 39} or particle morphologies.⁵⁶ Clearly the choice of precursor is crucial for obtaining fcc Ru. This has also been suggested by Kusada *et al.*,^{39, 57} who tested the hypothesis by using different Ru precursors (chloride, acetylacetonate and acetate) in the same reducing environment. Here the chloride yielded pure hcp phase whereas both the acetylacetonate and the acetate yielded phase pure fcc. The study by Ye *et al.*⁵⁸ has shown that it is possible to obtain the Ru fcc structure from a chloride precursor, which apparently contradicts the previous statement. However, their synthesis is based on heterogenous nucleation using seeded growth (Ru is deposited on a Pd seed). It is therefore reasonable that a different formation mechanism is observed compared with the homogeneous nucleation used here. When comparing the present data with *in situ* studies it is seen that the precursor also influences crystallite size with chloride precursors yielding larger particles than acetylacetonate precursors³⁷ at x = 0 and x = 1.

Another important factor is the choice of solvent, as demonstrated by Joo *et al.*⁵⁹ Ruthenium acetylacetonate was reduced in ethylene glycol yielding phase pure hcp Ru whereas reduction by ethanol plus triethylene glycol resulted in pure fcc Ru.^{37, 39} Using ethanol with butanediol produced mixtures of the two crystal phases.^{37, 58} This likely hinges on the reported temperature-controlled reaction behavior of organic solvents at solvothermal condition.³⁵

Elemental composition and morphology

EDX mappings of individual nanoparticles were performed for three samples ($x = 0.2, 0.5$ and 0.8) to investigate the elemental composition and distribution in the nanoparticles, **Figure 5**. Additional examples are presented in supporting information (**Figure S1**). The maps reveal an even distribution of the two elements for $x = 0.2$. For the two other samples the elemental distribution in the particles is mostly uniform although small fluctuations are seen. These might explain the small deviations of unit cell parameters seen in **Figure 3b** in the biphasic region. A similar trend was seen in a study by Hills *et al.*,⁶⁰ who reported broad difference in composition of Pt-Ru nanoparticles.

Figure 5. a-d) EDX of $\text{Pt}_{0.8}\text{Ru}_{0.2}$; e-h) EDX of $\text{Pt}_{0.5}\text{Ru}_{0.5}$; i-l) EDX of $\text{Pt}_{0.2}\text{Ru}_{0.8}$.

The morphology of the particles has been studied by TEM in all samples. The micrographs are shown in **Figure 6**. All samples in the range $x = 0.0 - 0.2$ exhibit spherical particle morphology; the alloying with ruthenium has no observable effect. This changes upon entering the biphasic region (from $x = 0.3$ and onwards) where some particles appear elongated (**Figure 6e-j**). Normally, these might be mistaken for separate particles; however, HR-TEM (**Figure 7**) confirm the presence of one, continuous particle with some stacking fault in between the elongated areas. The d -spacing for the different areas are shown in the dashed box in **Figure 7a**. They can be related to the d -spacing determined from the Rietveld/Le Bail refinements and be ascribed to either to the fcc (111) plane

($d_{111}=2.2$ Å) or the hcp (101) plane ($d_{101}=2.1$ Å). From this, the long flat end facets of the elongated particles could be determined to be {111} and {101} for fcc and hcp respectively.

The phase shift between hcp and fcc by a stacking fault requires only a small shift in stacking sequence. Similar kinds of staking faults have been reported for other types of compounds.⁶¹⁻⁶³ The observed stacking faults indicate that only a small energy difference separates the two crystal structures incurring easy transformation from one structure to the other. Indeed, it has been shown by DFT calculations that the energy difference between the hcp and fcc structures of Ru is small.⁵² This explains why it is possible for the two phases to co-exist across such a wide composition range. A similar effect can be found in a fcc structure, when a high concentration of twin planes are present, which break the ABCABC stacking order and mimics the ABABAB stacking order in hcp structure on the atomic level.⁶⁴ When a “chain” of elongated particles was analyzed by EDS line scan, **Figure 7c-d**, compositional fluctuation was identified across the row of particles. This can be correlated to the effects discussed above about imperfect alloying. The difference in stacking order between the fcc and hcp structures influences the nature of the facets at the surface of the particles, which can lead to different morphologies. This can explain why the morphologies change when the the hcp phase emerges for $x \geq 0.3$ as also demonstrated by Kambe *et al.*⁶⁵

Figure 6. TEM images a) $\text{Pt}_{1.0}\text{Ru}_{0.0}$ b) $\text{Pt}_{0.9}\text{Ru}_{0.1}$ c) $\text{Pt}_{0.8}\text{Ru}_{0.2}$ d) $\text{Pt}_{0.7}\text{Ru}_{0.3}$ e) $\text{Pt}_{0.6}\text{Ru}_{0.4}$ f) $\text{Pt}_{0.5}\text{Ru}_{0.5}$ g) $\text{Pt}_{0.4}\text{Ru}_{0.6}$ h) $\text{Pt}_{0.3}\text{Ru}_{0.7}$ i) $\text{Pt}_{0.2}\text{Ru}_{0.8}$ j) $\text{Pt}_{0.1}\text{Ru}_{0.9}$ k) $\text{Pt}_{0.0}\text{Ru}_{1.0}$. All the dashed boxes shows particles with internal phase shift due to stacking faults.

Figure 7. a) HR-TEM images of $\text{Pt}_{0.3}\text{Ru}_{0.7}$; d-spacing determined by FFT of the planes in the dashed box. b) Magnified region showing both hcp and fcc single domains with stacking faults at the boundaries. c) Line scan of the particle in the STEM image. d) STEM image green arrow indicate the direction of the line scan.

Conclusion

The relations between crystal phase and microstructural behavior has been established at the nanoscale for the $\text{Pt}_x\text{Ru}_{1-x}$ system. Crystallite and particle size were both found to decrease as the Ru content increased. The phase behavior of the system was found to deviate considerably from the bulk phase diagram and at the nanoscale the biphasic region is expanded to cover most of the phase diagram. The phase fractions produced are greatly influenced by the choice of precursor, solvent composition and synthesis parameters. As for the influence of precursor, it appears to be mediated by surfactant effects with acetylacetonate directing the product towards a metastable fcc state. Ultimately, this study has demonstrated the feasibility of employing continuous-flow synthesis for up-scale production of catalytic Pt-Ru nanoparticles, and elucidated options for “tailoring”, which are offered by controlled synthesis and alloying.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional results from Rietveld refinements, EDX mapping of selected samples, TEM size distributions.

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Graphical Abstract Figure