

Continuous Flow Synthesis, a Platform to Accelerate the Transition of Nanomaterials to Manufacturing

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ABSTRACT

Pt based alloy nanoparticles have extensive applications in industrial catalytic processes. In the last few decades, significant efforts have been devoted to the synthesis of metal and alloy nanoparticles with controlled size, composition and morphology, all of which have greatly improved activities in a variety of catalytic reactions. However, their application in real devices have been greatly hindered by the low availability of these materials. The attempts of scaling up using traditional batch process resulted in decreased control of critical reaction parameters, which showed inferior physical properties of the scaled up material and loss of its catalytic advantage. Continuous flow reactor technology offers an advanced platform to scale up these sensitive synthesis processes while at the same time gives the opportunity to investigate the fundamental nucleation and growth mechanisms time independently. In this paper, we show the synthesis of PtNi nanoparticles in continuous flow reactor and the effect of different solvents on the synthesis.

Keywords: PtNi nanoparticles, nanomaterials manufacturing, continuous flow synthesis, in-situ characterization, machine learning algorithm.

1 INTRODUCTION

Nanoscale materials and structures are common in nature and some of them have been used in industry for a long time. However, deliberately man-made nanostructures and materials have only recently advanced to industry and are slowly becoming commercialized. There is a lot of exciting research coming out of academic labs in recent years but the hard reality is that nanotechnology products are still rarely incorporated in existing applications [1]. The critical bottleneck in harvesting the benefits of advanced nanomaterials is their low availability [2]. One particular example is the development of nanocatalysts for fuel cell applications [3,4]. The industry still struggles to translate discovery lab inventions into tangible technological applications as nanomaterials are notoriously difficult to scale up to a commercial manufacturing level [5]. Large scale production in batch mode usually means much lower material quality and higher batch-to-batch variability [6].

Argonne's Material Engineering Research Facility is developing science-based reliable and reproducible manufacturing protocols for nanomaterials in continuous flow mode. This multidisciplinary project is aiming to investigate and better understand the fundamental processes that govern nucleation and particle growth in a continuous flow reactor system; phenomena that directly influence the resulting particle morphology and desired properties. Continuous flow microfluidic reactor technology is uniquely suited for nanomaterial synthesis. Particle size and morphology can be controlled via temperature, residence time, process chemistry, and precursor concentration. All these parameters can be easily and reproducibly controlled over extended time periods due to the superior and predictable mass, and heat transfer capabilities of a microfluidic reactor. The quantity of a material produced in a single batch is related to the reactor volume. In contrast, the quantity of a material produced in continuous flow mode depends only on the time the reactor is run. This is the key difference that helps to eliminate batch-to-batch variability. Continuous flow syntheses present multiple benefits over the traditional batch approaches: excellent solution homogeneity leads to narrow particle size distribution [7]; fully automated computer controlled system expedites nanoparticle synthesis optimization [8]; processes can be run in condition difficult or impossible to otherwise achieve; and scalable architecture provides the tools for seamless transition from benchtop processes to production.

Continuous flow reactions represent a new paradigm not only with respect to materials synthesis, but for time-resolved studies of reaction mechanisms [9]. Instead of monitoring reaction progress as a function of time, in continuous flow reactions, reaction progress is monitored as a function of distance along the flow path. The resolution with which the reaction is probed is largely independent of the kinetics of the reaction or the time-resolution of the measurement, but instead depends on spatial resolution of the probe along the beam path. The project is extensively utilizing Argonne's Advanced Photon Source in-situ material characterization capabilities and sophisticated machine-learning computational methods to develop a deep knowledge of the relationship between process parameters, nanoparticle morphology, physicochemical properties, and material performance.

While the initial focus of this effort is mostly on core/shell bi-metallic nanocatalysts for fuel cell application

[10], once developed, the ability to precisely control process parameters and to characterize flow reaction in-situ

using advanced X-ray tools combined with computational methods in a learning loop will allow for a quick

Solvents (ml)	Phenyl ether	Anisole	Tert-butylbenzene	α,α,α -Trifluorotoluene	Mesitylene	Diglyme
	4	4	4	4	4	4
Dichlorobenzene (ml)	0.6	0.6	0.6	0.6	0.6	0.6
Oleylamine (ml)	0.1	0.1	0.1	0.1	0.1	0.1
Oleic acid (ml)	0.1	0.1	0.1	0.1	0.1	0.1
Nickel acetate tetrahydrate (mg)	33.4	34.2	35.2	33.5	33.3	33.2
Platinum acetylacetonate (mg)	26.0	27.2	26.0	25.0	25.9	25.6
Tetradecanediol (mg)	17.0	17.3	17.7	16.8	16.9	16.9
Precursor solid	Observed	No	Observed	Observed	No	No
Solution appearance	Clear	Clear	Cloudy	Clear	Cloudy	Clear

Table 1: Solubility of reaction precursors in different solvents.

optimization of manufacturing procedures that can be readily extended to other material systems.

In order to investigate the particle nucleation and growth mechanism with in-situ X-ray tools at Argonne's Advanced Photon Source, we have to establish the base condition for the flow reactor. Here we show the synthesis of PtNi nanoparticles in a commercially available microfluidic flow reactor with back-pressure control that allows for reaction temperature well above boiling point of the solvent without expensive pressurized batch reactor. Under pressurized condition, we are able to investigate the effect and applicability of different common low boiling point solvents on the material morphology.

2 METHODS

All chemicals were of analytical grade and used as received. All the experiments were performed in a 1 ml volume microfluidic reactor with back pressure of 10 bar on a Asia flow reactor system. Reaction solutions were purged with Ar flow for 30 min to remove dissolved oxygen before pumping into the microfluidic reactor.

2.1 Solubility of reaction precursors

For the batch synthesis, reaction precursors were soluble in the reaction solvents at reaction temperature of 200 °C. For flow reactor synthesis, reaction precursors should be dissolved in reaction solvents at room temperature in order to achieve a uniform solution composition in the microfluidic reactor. The reaction precursors were dissolved in different solvents with the same precursor/ solvent/ surfactant/ reducing agent ratio at 110 °C and the reaction

mixture was then cooled down to room temperature overnight in order to check the solubility. As shown in Table 1, precursors are soluble in anisole, mesitylene, and diglyme but only partially dissolved in the solvent of original synthesis (phenyl ether) and also in tert-butylbenzene or α,α,α -trifluorotoluene. In addition, the solution was cloudy when tert-butylbenzene or mesitylene were used because of the separation of water from the hydrated nickel precursor in these solvents. As water can be removed by purging argon into the solution at 110 °C, the cloudiness of the solution would not be a problem for the flow reactor. However, the poor solubility of the metal precursors in phenyl ether, tert-butylbenzene and α,α,α -trifluorotoluene at room temperature is a more difficult challenge to overcome.

2.2 Characterization of PtNi nanoparticles

PtNi nanoparticles were separated from the post-reaction mixture by centrifugation in hexane and ethanol solvents. A suspension of PtNi nanoparticles in hexane was drop-cast onto a copper grid for transmission electron microscopy (TEM) characterization, performed on a JEM-2100F at the Center for Nanoscale Materials (Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357) at Argonne. The compositions of the PtNi nanoparticles were determined by energy dispersive X-ray (EDX) spectroscopy attached on the JEM-2100F TEM.

3 RESULTS AND DISCUSSIONS

The TEM and EDX results of PtNi nanoparticles synthesized using a batch process in a flask using phenyl ether as solvent are shown in Figures 1a and 1d. As seen in the TEM image, monodispersed particles with a size of around 5 nanometers (nm) are prepared after a 30 min reaction time at 200 °C. The composition of the particles are determined to be Pt and Ni with ratio of 1:1, as shown in Figure 1d and 1g. The TEM and EDX results of PtNi nanoparticles synthesized in the flow reactor using phenyl ether are shown in Figure 1b, 1c and 1e, 1f. The conditions (temperature and flow rate) of the flow reactor synthesis were stabilized for 30 min before taking the first sample-Flow 1. The second sample-Flow 2 was collected after 30 min, in order to check the particle quality as a function of time. As shown in Figure 1b, PtNi nanoparticles are slightly larger than those from batch synthesis and less monodispersed. The composition of the PtNi nanoparticles is slightly different from batch synthesis with less Ni in the Flow-1 sample (47%). In the Flow-2 sample, the PtNi nanoparticles are similar to the Flow-1 material, although they are less monodisperse with even lower Ni content (40%).

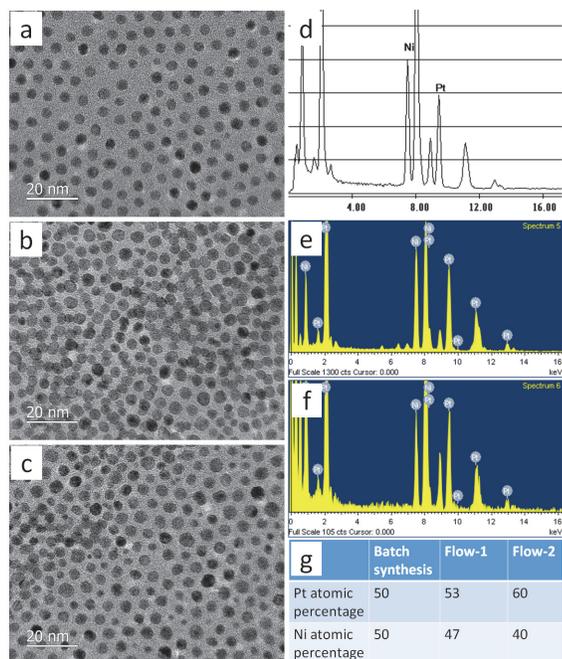
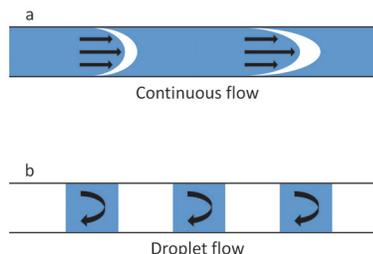


Figure 1: TEM images and EDX spectroscopy results of PtNi nanoparticles synthesized in batch (a and d) and flow reactor (b, e for Flow-1 and c, f for Flow-2) using phenyl ether as solvent; g, atomic ratio between Pt and Ni from EDX.

The less monodispersed particle size distribution is very likely caused by the temperature and concentration gradients in the continuous flow mode as shown in Scheme 1 and may be solved by switching to droplet flow mode [7].

The decrease of the Ni content in Flow-2 particles is caused by the poor solubility of the Ni precursor in phenyl ether at room temperature as shown in Table 1.



Scheme 1: Difference between continuous flow mode and droplet flow mode in a flow reactor.

We observed an increased amount of Ni precursor precipitation over time in the flow reactor synthesis as the initial temperature of the feed solution slowly cooled down. In order to solve this solubility problem, one may switch to other solvents, decrease the precursor concentrations or pre-heat the precursors. While the first two methods may change the reaction chemistry, the last one is operationally complex.

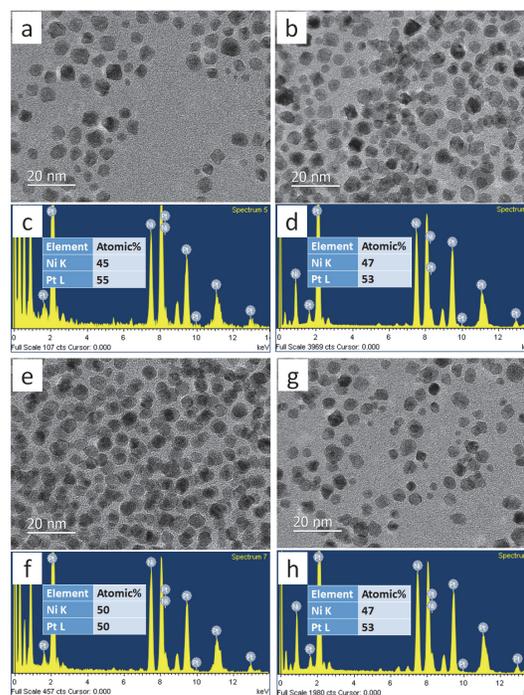


Figure 2: TEM images and EDX spectroscopy results of PtNi nanoparticles synthesized in flow reactor using diglyme as solvent. a, c and b, d, two samples with 30 min interval at 200 °C for 30 min reaction; e and f, 200 °C for 10 min reaction; g and h, 220 °C for 10 min reaction.

Using diglyme as solvent and 10 bar back pressure, we were able to run the synthesis of PtNi nanoparticle in flow reactor at 200 and 220 °C. The TEM and EDX results are shown in Figure 2. With a high precursor solubility in

diglyme, the changing of particle composition as a function of time was not observed. This result demonstrates the advantage of a flow reactor in control of process parameters in nanomaterial scale up. However, the PtNi nanoparticles obtained in diglyme were not as spherical as those obtained in phenyl ether. This means a preferential facet growth may be promoted in diglyme due to altered interactions between the surfactants and particle facets. As shown in Figure 2e, PtNi nanoparticles produced at a 10 min reaction time are more spherical. This indicates the preferential facet growth may not have started at early stages, which is probably form spherical particles at shorter reaction time. However, the reaction yield at shorter reaction times may be decreased.

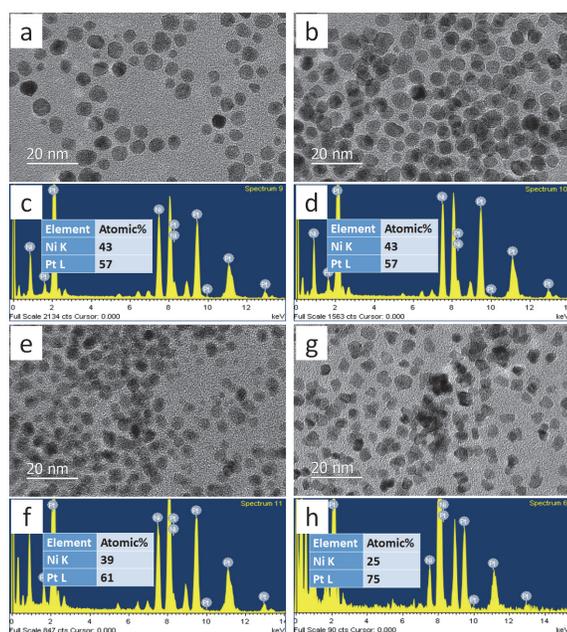


Figure 3: TEM images and EDX spectroscopy results of PtNi nanoparticles synthesized in flow reactor (a-f) and batch synthesis (g and h) using mesitylene as solvent. a, c and b, d, two samples with 30 min interval at 200 °C for 30 min reaction; e and f, 200 °C for 10 min reaction; g and h, 165 °C for 60 min reaction.

Shown in Figure 3 are TEM and EDX results of the PtNi nanoparticles synthesized in flow reactor using mesitylene as solvent with 10 bar back pressure. Similarly to diglyme, the particle composition and the size do not change with time due to good precursor solubility. This result further proves the advantage of process control in flow reactor. PtNi nanoparticles made in mesitylene have similar spherical morphology with those in diphenyl ether but show a slightly larger particle size. As shown in Figure 3e, the particle size is smaller for 10 min reaction. This means the particle size can be controlled by reaction time. In-situ X-ray experiments may help understand the particle formation mechanism and guide the control of particle size and composition without sacrificing the yield. High back pressure in a flow reactor allows the use of low boiling

solvents at high temperatures. The TEM and EDX results using lab flask are shown in Figure 3g and 3h. Without pressure, the reaction can only run at 165 °C and produce particles with irregular shape and less Ni content.

4 CONCLUSIONS

Different solvents were used in a flow reactor to investigate their effect on the synthesis of PtNi nanoparticles and particles morphology. The usability of continuous flow reactor for nanomaterial scale up was demonstrated. The back pressure function of microfluidic continuous flow reactor enables the use of low boiling point solvents at high temperature without losing control of morphology and particle size. This work establishes a solid starting point for the next step investigations involving in-situ X-ray and machine learning components.

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