

Cost-Responsive Optimization of Nickel Nanoparticle Synthesis

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Early-stage cost evaluation during catalyst development holds the potential to accelerate the commercialization and deployment of advanced catalytic materials for sustainable chemical processes. The modeling and assessment of manufacturing costs as early as the laboratory synthesis scale, for example, focusing on materials costs and synthesis performance metrics, can support the development of an experimental–economic feedback loop that enables rapid insight into cost drivers associated with catalyst synthesis and highlights areas that require focused research and development effort. Ultimately, this feedback loop supports the realization of an economic understanding of the overall synthetic process and highlights opportunities to reduce costs, serving as the foundation for the scale-up of catalyst manufacturing. Herein, a case study is presented utilizing CatCost, a free and publicly available estimation tool for the evaluation of catalyst manufacturing costs, to perform a cost-responsive optimization of the synthesis of nickel nanoparticles (Ni NPs). It is demonstrated that reagent substitutions with more cost-effective analogs, coupled with stoichiometric optimization, afford a 58% reduction in raw materials cost without changing the product yield or properties.

materials that drive essential catalytic transformations.^[1–3] However, despite frequent references to cost when introducing the aims of a research effort, published research studies that undertake synthetic improvements and method development in direct response to specific, quantitative cost information remain rare.^[4] The scarcity of published cost-integrated research can be attributed to challenges in the availability of reagent cost information at large scales, as well as a lack of information on manufacturing operations.^[5] Addressing these gaps and enabling the use of cost-responsive research and optimization could drive more efficient research and development (R&D) by incorporating valuable cost and commercialization information earlier in the process. The early-stage assessment of catalyst manufacturing costs can guide decision making, provide critical insight into primary cost drivers, and focus efforts on methods for reducing


1. Introduction

Catalysis researchers increasingly consider materials cost early in their development of catalysts for chemical, biological, and materials reactions, starting with small-scale fundamental investigations of new catalytic materials and continuing as catalytic reactions progress toward commercial maturity. For example, a longstanding goal in the catalysis community is the replacement of expensive precious metal catalysts with more cost-effective options, such as abundant, first-row transition metals, to combat current and future challenges in the cost and availability of

these costs. Further, catalysis is a key driver of efficiency in the production of fuels for transportation and chemical products for plastics, packaging, pharmaceuticals, and other consumer goods. Research into improved catalysts, especially when it enables decarbonization and improved efficiency for the energy and chemicals sectors, directly addresses U.N. Sustainable Development Goals (SDGs) 7: Affordable and Clean Energy, 9: Industry, Innovation and Infrastructure, and 13: Climate Action. Studies, like this one, that support more efficient, market-informed research and development can help accelerate the development of critical sustainable technologies and do so at lower cost, indirectly addressing SDGs 8: Decent Work and Economic Growth, and 12: Responsible Consumption and Production.

Toward this end, we have developed CatCost™, a free catalyst cost estimation tool that features comprehensive methods for understanding and quantifying components of catalyst cost.^[4,6] CatCost considers raw materials purchase costs, capital and operating expenditures (CapEx and OpEx, respectively), and the value and/or cost of spent catalysts at the commercial scale, offering researchers opportunities to adapt their synthetic methods and reducing cost while improving commercial viability. We recently demonstrated the application of CatCost to catalyst selection for catalytic biomass conversion, by comparing zeolite, metal-on-metal oxide, and metal carbide catalysts at varying production scales and across multiple dimensions of performance, cost, and environmental impact.^[4] The analysis revealed that an early-stage

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0.5% Pt/TiO₂ catalyst offers a 40-fold reduction in averaged environmental impact and 50% lower cost per gallon of fuel product compared to a commercial zeolite catalyst while improving performance. We have also published a cost-informed optimization of a colloidal Pt nanoparticle (NP) synthesis in an ionic liquid (IL) solvent.^[7] This study showed that IL solvents, which are frequently much more costly than conventional organic solvents but offer synthetic benefits, can be cost-competitive with conventional solvents if recycled. These studies exemplify the decision-making benefits of incorporating cost insight early in the development of novel catalysts and are particularly impactful for newer manufacturing methods not yet practiced for commercial catalyst production. Ultimately, these types of investigations could offer a roadmap for faster commercialization of breakthrough technologies.

In this work, we present a straightforward example of cost-responsive synthetic modifications, using CatCost to optimize the synthesis of nickel NPs. Over the past few decades, Ni NPs have shown excellent catalytic activity in a wide range of applications including biomass conversion, proton reduction, and hydrogenation.^[8-9] Carencio et al. reported a ubiquitous solution-phase method for the isolation of phase-pure, monodisperse colloidal Ni NPs with average diameters of 11.0 ± 1.0 nm in 80% yield.^[9] Although high-yielding and reproducible, this method uses relatively expensive Ni^{II} and phosphine precursors that may hinder the implementation of these materials in larger-scale commercial processes. Herein, we demonstrate a case study using CatCost to inform the optimization of Ni NP synthesis toward a more sustainable and scalable route. By coupling economic analyses with experimental assessment and optimization, an alternative synthetic approach to prepare phase-pure, colloidal Ni NPs was developed. In particular, substitution of Ni(acac)₂ and trioctylphosphine (TOP) with relatively low-cost congeners, Ni(OAc)₂ and PPh₃, respectively, as well as a systematic evaluation of the impact of the Ni^{II}:PPh₃ molar ratio, resulted in the formation of Ni NPs with similar properties (i.e., size morphology) to those of the method by Carencio et al.,^[9] albeit with yields up to 25% greater than previously reported for PPh₃-stabilized Ni NPs.^[10] By simply replacing the high-cost precursors, a 58% reduction of the estimated materials cost was realized, affording a net reduction of the raw materials contributing to the overall process cost by \$67/kg catalyst. Finally, sensitivity analysis on the price variability of the Ni NP reaction revealed that the main contributors to catalyst purchase cost uncertainty were synthesis yield and target wt.% loading. In addition, by simply substituting Ni(acac)₂ and TOP with Ni(OAc)₂ and PPh₃, respectively, a modeled 72% reduction in raw materials cost could be achieved. These results, and the approach highlighted herein, offer a framework for the development and optimization of cost-responsive synthetic processes.

2. Results and Discussion

To begin our study of utilizing economic analyses to drive procedural optimization(s) of colloidal nanomaterials, Ni NPs were first synthesized according to a previously reported procedure.^[9] Briefly, Ni NPs were prepared via the thermal decomposition of nickel(II) acetylacetonate (Ni(acac)₂, 7.8 mmol, 1 eq) at 220 °C for 2 h in the presence of trioctylphosphine (TOP, 0.5 eq), oley-

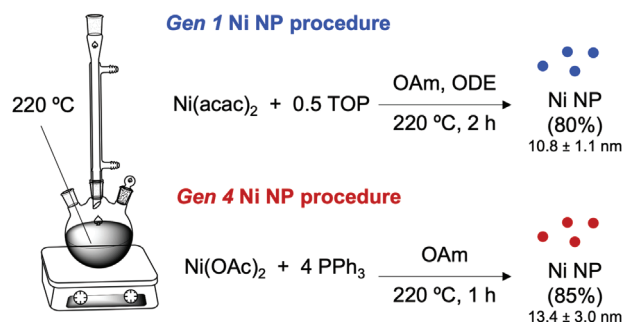


Figure 1. Initial (top, blue) and optimized (bottom, red) procedures for the synthesis of colloidal Ni NPs.

lamine (OAm, 10 eq), and octadecene (ODE, 0.8 eq) (Figure 1). Following washing and centrifugation, 313 mg of phase-pure Ni NPs were obtained, resulting in an 80% Ni NP yield (Figure S1, Table 1). Transmission electron microscopy (TEM) imaging revealed polycrystalline spherical Ni NPs with an average size of 10.8 ± 1.1 nm, consistent with those previously reported (Figure 2a).^[9] This set of reaction conditions (i.e., reagents and stoichiometries) and physical property characterization data (i.e., particle size, morphology, yield) serve as the basis for the cost-responsive optimization study.

The synthesis-driven cost analyses for Ni NPs reported in this study were created to provide actionable insight to optimize a synthetic protocol at the laboratory scale. Accordingly, the analysis is based directly on the methods used in the experimental synthesis, similar to our previous IL recycling study, with a focus on materials and synthetic conditions.^[7] This is in contrast to more mature techno-economic analyses that focus on the translation of laboratory-scale procedures to the more scalable methods of commercial catalyst manufacture.^[4] The preliminary economic evaluations conducted herein were focused on elucidating costs that could reasonably be addressed with changes to the experimental procedure, namely, raw materials and their stoichiometries, to create an experimental–economic feedback loop that could provide rapid insight into cost drivers associated with Ni NP synthesis. Capital and operating costs were excluded from the analyses, as they are beyond the scope of this study focused on modification of laboratory-scale parameters. Furthermore, the modeled costs of traditional laboratory methods for colloidal nanoparticle syntheses are exceptionally high, especially when the methods are not replaced with more industrially relevant approaches (i.e., continuous flow instead of batch) and when the volumetric scale of the batch process is preserved (as it is well known that scaling NP reactions volumetrically can have deleterious effects on product fidelity).^[11-15] In consequence, capital and operating costs of laboratory NP syntheses can dramatically exceed the purchase cost of the materials.^[7] For example, the total cost for Ni NPs synthesized with the Carencio procedure^[9] was estimated to be \$47765/kg catalyst. Direct operating costs such as labor and maintenance contribute to the bulk (ca. \$22800/kg) of the cost of the low-throughput batch reaction (Figure S2, Supporting Information). While outside of the scope of the analyses described herein, we have included the CapEx and OpEx summary outputs and complete estimate files in Figures S2,S3 (Supporting Information). A thorough

Table 1. Consequence of precursor replacement(s) on Ni NP yield, size, and materials cost per kg catalyst.

Catalyst	Metal, Ligand [eq]	Ni NP yield ^{a)}	Size [TEM, nm] ^{b)}	Materials cost [\$ /kg catalyst] ^{c)}
Gen 1	Ni(acac) ₂ , TOP (0.5)	80.1%	10.8 ± 1.1	\$116.25
Gen 2	Ni(OAc) ₂ , TOP (0.5)	1.3%	11.1 ± 2.8	\$6691.16
Gen 3	Ni(OAc) ₂ , PPh ₃ (0.5)	-	16.0 ± 1.5	-
Gen 4	Ni(OAc) ₂ , PPh ₃ (4)	85.4%	13.4 ± 3.0	\$49.19

^{a)} Ni NP yield determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES); ^{b)} Size distribution was determined from a manual measurement of the particle diameter for >100 particles; ^{c)} Materials cost (\$/kg catalyst) includes NiII precursor, phosphine ligand, OAm, ODE (Gen 1 only), workup solvents (Gen 1- acetone, chloroform, Gen 2, 4 – isopropanol, chloroform), and SiO₂ support.

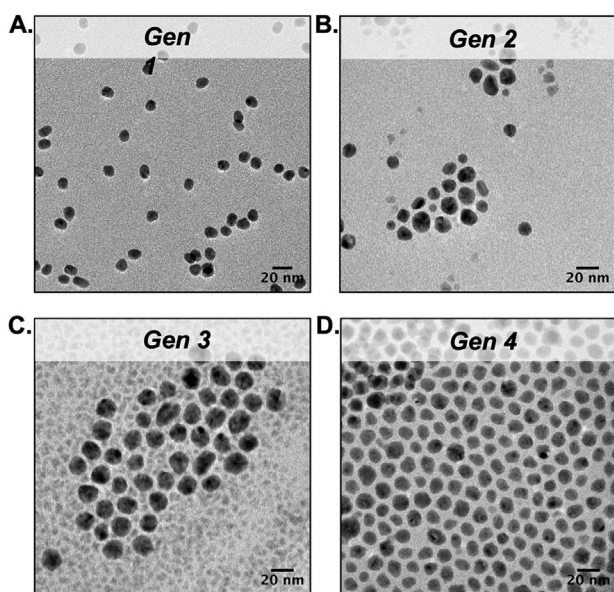


Figure 2. Representative TEM images of A) Gen 1, B) Gen 2, C) Gen 3, and D) Gen 4 Ni NPs.

examination of methods to reduce the operating cost of nanoparticle syntheses through the utilization of continuous flow synthesis methods is the focus of an upcoming manuscript.

A materials cost analysis of the previously reported Ni NP procedure (vide supra), hereafter referred to as Gen 1, identified that the three most significant drivers of total materials cost (\$116.25/kg catalyst) are: the Ni^{II} precursor (Ni(acac)₂, \$8.21/kg catalyst, 7%), the OAm surfactant (\$16.02/kg catalyst, 14%), and the TOP ligand (\$82.73/kg catalyst, 71%; **Figure 3A**). Overall, these three cost drivers constitute 92% (\$106.96/kg catalyst) of the materials cost and thus present a significant opportunity for cost reduction. Given that the OAm surfactant is widely recognized as an essential component in the synthesis of colloidal NPs (i.e., it influences the kinetics of M²⁺ reduction and stability),^[9,11] the metal precursor and phosphine ligand were identified as more amenable for replacement.

Previously reported Ni NP syntheses have utilized a range of precursors including Ni(acac)₂,^[12-14] nickel nitrate (Ni(NO₃)₂ · 6H₂O),^[15-18] and nickel acetate (Ni(OAc)₂ · 4H₂O).^[17-19] As shown in **Figure 3B**, the Ni(acac)₂ used in the Gen 1 protocol is the most expensive of these Ni^{II} precursors at \$29.17/kg. While Ni(NO₃)₂ has the lowest price, representing a 2.8-fold price reduction com-

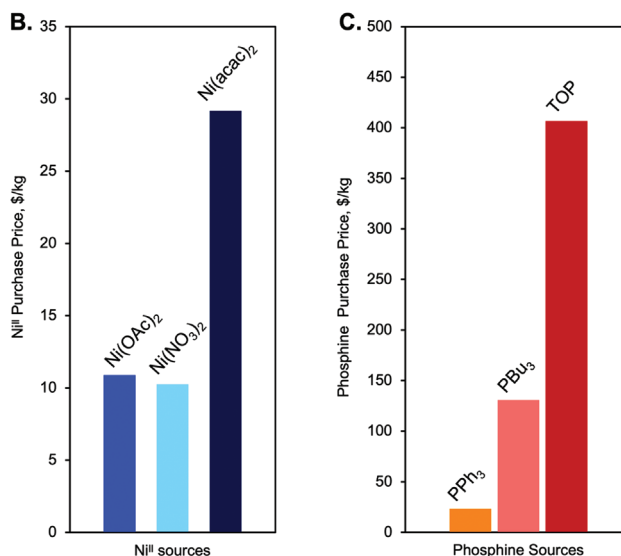
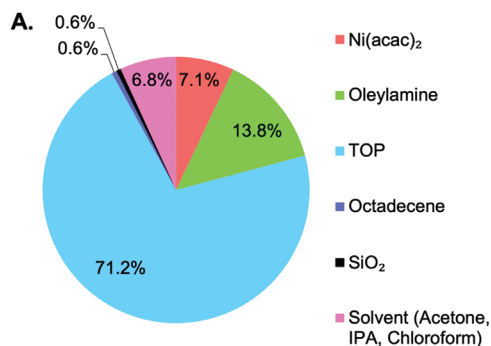


Figure 3. A) Materials-based cost drivers (\$/kg catalyst) of the Gen 1 procedure. Average B) Ni^{II} precursor and C) phosphine ligand purchase costs (\$/kg reagent) determined through public and proprietary sources.

pared to Ni(acac)₂, the nitrate salt has poor solubility in the organic reaction mixture. As a result, Ni(OAc)₂ (\$10.88/kg) was identified as the most suitable candidate to replace the high-cost Ni(acac)₂ without requiring a change to the organic reaction mixture. Similarly, while procedures for Ni NPs generally utilize TOP as the stabilizing ligand,^[11,14-16] tertiary phosphines (PR₃; e.g., R = butyl (Bu),^[10,20] phenyl (Ph)^[10]) have also been shown to stabilize Ni NPs, albeit at lower yields of 60%.^[10] Comparing the reagent costs of the series of stabilizing ligands revealed that

PPh_3 is significantly more cost-effective at \$23.34/kg compared to TOP (\$406.60/kg) and PBu_3 (\$131.00/kg, Figure 3C). Combining the replacement of $\text{Ni}(\text{acac})_2$ with $\text{Ni}(\text{OAc})_2$ and TOP with PPh_3 suggests that a 72% reduction in cost per kg catalyst could be expected, assuming these materials could be substituted into the existing synthesis with no change to yield or product quality.

With a set of materials substitutions identified to reduce the NP manufacturing cost, the next step in this cost-informed synthetic optimization was to experimentally evaluate the modifications suggested by economic analyses. Substitution of the Ni^{II} precursor and ligand in the Gen 1 procedure was systematically assessed to investigate the resulting Ni NP yield, purity, size, and polydispersity. First, the Gen 1 reaction was modified by the simple substitution of $\text{Ni}(\text{OAc})_2$ in place of $\text{Ni}(\text{acac})_2$ (Gen 2), accompanied by some minor changes to the reaction procedure (ODE was omitted and the reaction was heated for 1 h instead of 2 h). The resulting Gen 2 Ni NPs were similar in diameter to those of Gen 1 Ni NPs, however, a greater variation in morphology was observed. The Gen 2 synthesis produced Ni spheres, cubes, and rods, as determined by TEM (Figure 2b, Table 1), whereas the Gen 1 synthesis resulted in spherical particles only (Figure 2a). Moreover, the NP yield was dramatically reduced from 80% to $\approx 1\%$, with the majority of the material being lost in the form of a non-dispersible bulk aggregate. The significant reduction in the yield results in a cost increase of over 3 orders of magnitude relative to the Gen 1 procedure (total materials cost; \$6691.16/kg catalyst). Collectively, the substantial cost increase due to the reduced yield from this single reagent substitution highlights the importance of coupling early-stage economic evaluation with experimental validation. While a significant cost reduction was expected based on preliminary cost estimates, the synthetic consequences of a reagent substitution could not be considered by such a model and required experimental validation.

As discussed above, the price determination of substitute phosphines revealed that PPh_3 has a 17.8-fold price decrease compared to that of TOP. Accordingly, cost evaluation of TOP substitution for this relatively inexpensive ligand showed \$88.22/kg catalyst cost reduction relative to Gen 1, assuming an 80% Ni NP yield (\$28.17/kg catalyst). To experimentally probe whether these reagent substitutions would generate Ni NPs with properties and yields similar to those obtained from the Gen 1 procedure, $\text{Ni}(\text{acac})_2$ and TOP were replaced with $\text{Ni}(\text{OAc})_2$ and PPh_3 (0.5 eq), respectively (Gen 3). As with the Gen 2 conditions, the reaction primarily resulted in the formation of insoluble aggregate, and a negligible quantity of dispersible Ni NPs were isolated. In addition, those particles that could be recovered from the reaction mixture were found to be significantly larger than those of the Gen 1 base case, with an average particle size of 16.0 ± 1.5 nm as determined by TEM. As noted above, this highlights the importance of an experimental–economic feedback loop that reveals the consequences of both experimental procedure modification and the process cost estimate. Since prior optimization experiments by Carencu et al. revealed that small changes in the TOP: Ni^{II} molar ratio affected the NP size, dispersity, and yield,^[9] we conducted a series of reactions to investigate the influence of PPh_3 : Ni^{II} on Ni NP yield and properties. Increasing the PPh_3 : Ni^{II} to 4 (Gen 4) resulted in the formation of phase-pure colloidal Ni NPs with an average diameter of 13.4 ± 3.0 nm (Figure 2d, Figure S1, Supporting Information). Furthermore, a Ni NP yield of

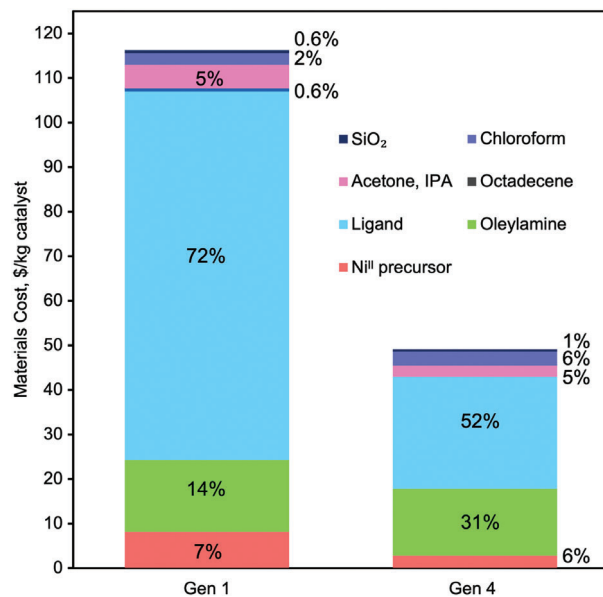


Figure 4. Contribution of major cost drivers (\$/kg catalyst) to total materials cost for Gen 1 (left) synthesized with $\text{Ni}(\text{acac})_2$ and TOP and Gen 4 (right) prepared with $\text{Ni}(\text{OAc})_2$ and PPh_3 as substitute reagents.

85% was obtained, which is 25% higher than that achieved in the previously reported synthesis of PPh_3 -stabilized Ni NPs.^[10] The maintenance of a high yield (85%) enabled the realization of the estimated cost savings afforded by the low-cost reagents for a total materials cost of \$49.19/kg catalyst. This marks an overall materials cost reduction of 58% in comparison to the base Gen 1 reaction (Figure 4). Moreover, these results confirm that an iterative feedback loop investigating the consequence of procedure modification on both the material properties and cost can result in the development of alternative, cost-effective methods for nanomaterial syntheses. Here, integration of economic information with chemical iteration resulted in (1) a decrease in total materials cost per kg catalyst through the use of relatively low-cost reagents, while (2) maintaining the average Ni NP size and morphology, and (3) increasing the Ni NP yield compared to previously published results with comparable reagents. Overall, these types of rapid, early-stage analyses could accelerate the development of sustainable routes for the manufacture of advanced nanostructured catalysts.

With final, cost-guided conditions determined for the synthesis of Ni NPs using relatively inexpensive precursors, we sought to assess the impact of the variability of the critical materials cost drivers discussed above (i.e., reagent and catalyst support costs) as well as reaction performance metrics (i.e., catalyst yield, target weight loading (wt.%) on the raw materials costs. These sensitivity analyses were conducted using the raw materials cost of the Gen 1 procedure as the baseline scenario. Although not evaluated experimentally, the sensitivity of Ni wt.% loading (e.g., Ni/SiO_2) on the materials cost was included to assess the impact of utilizing a range of catalytically relevant loadings that could easily be tailored by adding differing amounts of support for the target application. The tornado plot summarizing the sensitivity analysis is presented in Figure 5. Additional information including

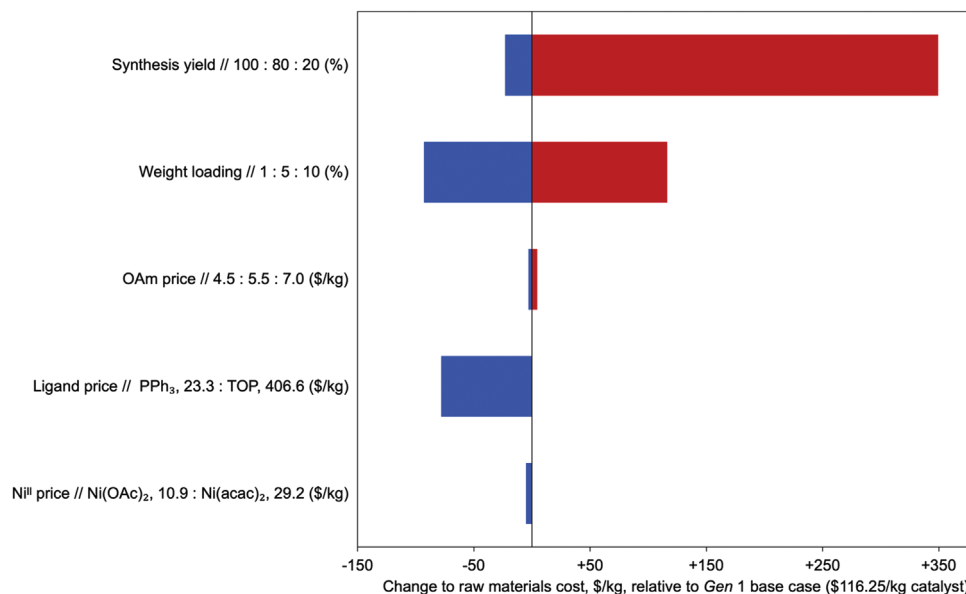


Figure 5. Tornado plot summarizing the sensitivity of the change to raw materials cost or performance metrics relative to the base scenario (Gen 1). Reagents with relative changes to material cost $\leq \pm 1\%$ were omitted.

the sensitivity analysis assumptions and the high and low input values for the reagents are in Supporting Information.

The two largest contributors to uncertainty in the cost of the Ni NP procedure were the performance metrics, including synthesis yield and target wt.% loading. Given that variation of the synthesis yield directly influences the final catalyst mass, changing the Ni NP yield from the baseline (80%) to low (20%) or near-quantitative resulted in significant changes to the procedure cost, spanning between $\approx -20\%$ to $+300\%$. These results are consistent with the experimental-economic evaluations conducted above, where for example, the reduction in yield of the Gen 2 Ni NPs resulted in a significant escalation of the materials cost (Table 1). As such, sustaining a high Ni NP yield throughout synthetic modifications is critical for maintaining a low overall raw material cost contribution to the overall catalyst manufacture cost. Likewise, estimated relative costs ranging from -80% to $+100\%$ were observed based on changes to the target wt.% Ni/SiO₂ from 1 to 10 wt.%. A large relative cost change of -67% was estimated with the replacement of TOP in the base scenario with PPh₃. Finally, the substitution of Ni(acac)₂ with Ni(OAc)₂ showed a $\approx -4\%$ change in raw materials cost. Taken together, these results show that the exchange of the materials cost drivers with more cost-effective reagents could amount to a -72% change in raw materials cost, assuming no change to NP yield or product quality. Although this was not experimentally achieved in the Ni NP synthesis here, these results confirm that early-stage economic assessment of materials cost drivers could provide guidance for determining procedure modifications that would afford decreased materials costs. Relatively small changes to materials costs were observed with variability in OAm price, which was determined to be on the order of $\approx -3\%$ to $+4\%$. The remaining reagents, including the SiO₂ support and ODE (Gen 1 only), resulted in variations in materials price of $\leq \pm 1\%$. Overall, these variability studies reveal that process cost reduction on the order of $\approx -20\%$ to -80% , relative to the base Gen 1 raw materials cost, could be realized with

an improvement of the performance metrics or ligand replacement. Finally, it is important to note that the reaction time was decreased from 2 h (Gen 1) to 1 h in the Gen 4 protocol which has no influence on the materials cost drivers or performance metrics but would significantly influence the overall catalyst cost (i.e., including capital and operating costs in addition to materials costs) as shortening the reaction duration would directly influence the system throughput. While outside of the scope of this study, an evaluation of the full cost of Ni NP synthesis, including capital and operating components, as well as opportunities to reduce cost by replacing batch methods with continuous flow, is forthcoming.

3. Conclusion

Herein, we demonstrate the utility of employing early-stage cost estimation to guide the optimization of catalyst synthesis procedures to more economical solutions. Utilizing an experimental-economic assessment feedback loop, we developed a cost-responsive optimization of the synthesis of Ni NPs through the systematic evaluation of traditional reagent substitutions and the associated change in catalyst cost. Replacement of the metal precursor and ligand from Ni(acac)₂/TOP (1:0.5 eq) to Ni(OAc)₂/PPh₃ (1:4 eq) resulted in a 58% reduction of the estimated raw materials cost, affording a more cost-effective method for the production of Ni NPs at a commercial scale. A sensitivity analysis was performed to examine the influence of various input parameters on the catalyst purchase cost. These results revealed the main cost contributors are synthesis yield and target wt.% loading, which could result in estimated cost changes on the order of $\approx -80\%$ to $+300\%$ relative to the base case scenario. Overall, this case study shows that cost information is most useful when integrated with chemical insight and iteration throughout synthetic R&D and demonstrates that incorporating cost evaluation into process development could inform steps toward decreasing

the overall cost of catalyst manufacture. This analysis framework, coupled with a detailed life cycle assessment can be applied to various catalyst design scenarios to support the decision-making process at all stages of catalyst R&D and commercialization.

4. Experimental Section

Synthetic manipulations to prepare the nanoparticles were conducted under a N₂ atmosphere using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox unless otherwise noted. Oleylamine (70%) and Octadecene (90%) were purchased from Sigma-Aldrich and used as received. Nickel (II) acetylacetonate (Ni(acac)₂) was purchased from Strem Chemicals and Nickel (II) acetate tetrahydrate (Ni(OAc)₂) was purchased from Acros Organics and used as received. Trioctylphosphine (TOP) and triphenylphosphine (PPh₃) were purchased from Sigma Aldrich and used as received.

Solution Phase Synthesis of Ni NPs with Ni(acac)₂ and TOP (Gen 1): The synthesis of Ni NPs using Ni(acac)₂ and TOP was performed according to a previously published procedure.^[9] A 3-neck round-bottom flask fitted with a condenser and two septa was charged with Ni(acac)₂ (2.0 g, 7.8 mmol, 1 eq), OAm (25.6 mL, 77.8 mmol, 10 eq), and ODE (2.0 mL, 6.3 mmol, 0.8 eq). Following three evacuation/N₂ cycles, the apparatus was heated rapidly to 100 °C under vacuum and maintained at this temperature under vacuum for 1 h. Then the heat source was removed, and the reaction mixture was allowed to cool to ambient temperature naturally. Once the mixture reached room temperature, the apparatus was refilled with an N₂ atmosphere, and TOP (1.74 mL, 3.9 mmol, 2 eq) was added to the reaction vessel. Following three evacuation/N₂ cycles, the apparatus was heated rapidly to 220 °C and maintained at this temperature for 2 h before the heat source was removed and the reaction mixture was allowed to cool to ambient temperature. To the cooled reaction mixture, 40 mL acetone was added to precipitate the nanoparticles, which were then separated by centrifugation at 8000 RPM for 10 min.

Solution Phase Synthesis of Ni NPs with Ni(OAc)₂ and PPh₃ (Gen 4): A 3-neck round-bottom flask fitted with a condenser and two septa was charged with Ni(OAc)₂ (0.97 g, 3.9 mmol, 1 eq) and OAm (12.8 mL, 38.9 mmol, 10 eq). Following three evacuation/N₂ cycles, the apparatus was heated rapidly to 100 °C under vacuum and maintained at this temperature under vacuum for 1 h. Then the heat source was removed, and the reaction mixture was allowed to cool to ambient temperature naturally. Once the mixture reached room temperature, the apparatus was refilled with an N₂ atmosphere and PPh₃ (4.08 g, 15.6 mmol, 4 eq) was added to the reaction vessel. Following three evacuation/N₂ cycles, the apparatus was heated rapidly to 220 °C and maintained at this temperature for 1 h before the heat source was removed and the reaction mixture was allowed to cool to ambient temperature. To the cooled reaction mixture, CHCl₃ (≈5 mL) was added to assist in the transfer of the cooled reaction mixture to a centrifuge tube. A 20 mL portion of isopropanol was added to precipitate the nanoparticles, which were then separated by centrifugation at 8000 RPM for 10 min.

Synthesis of Silica-Supported Ni NPs (Ni/SiO₂): The recovered Ni NPs were redispersed in 10 mL of CHCl₃ and added dropwise to a suspension of silica support in CHCl₃ (1 g mL⁻¹), in order to yield a catalyst with 5 wt.% Ni NP loading. The mixture was sonicated for 5 min and stirred overnight. The resulting catalyst was separated via centrifugation, dried in a vacuum, and stored under an N₂-filled glovebox.

Characterization: Powder X-ray diffraction (XRD) measurements were performed using a Rigaku Ultima IV diffractometer with a Cu Kα source (40 kV, 44 mA). Diffraction patterns were collected in the 2θ range of 20–100° at a scan rate of 4° min⁻¹. Diffraction patterns were compared to powder diffraction files of the reference materials from the International Centre for Diffraction Data (ICDD). Samples for TEM were drop-cast onto carbon-coated copper grids (Ted Pella part no. 01824). Imaging was performed using a FEI Technai G2 ST20 TEM operating at 200 kV. All image analyses were conducted with ImageJ software.^[21] Size distributions were determined from a manual measurement of > 100 of the isolated crystalline domains.

Catalyst Cost Estimation: Cost estimates were compiled in Microsoft Excel v.16 using the spreadsheet version of CatCost v.1.1.0.^[6] A full description of assumptions, including input costs, cost factors, and other variables, is provided in the Supporting Information, particularly in Tables S1–S3 (Supporting Information). All prices were adjusted to 2016 U.S. dollars (USD) using the U.S. Bureau of Labor Statistics Chemical Producer Price Index.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords

catalysis, CatCost, nanomaterials, synthesis, techno-economic analysis

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