

Palladium/Alginate/Poly(NIPAM) Beads with Thermally Tunable Hydrophobic–Hydrophilic Domains for Nitroarene Reduction Reactions in Aqueous Media

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ABSTRACT: This study introduces a thermoresponsive hybrid hydrogel catalyst that integrates a poly(*N*-isopropylacrylamide) (poly(NIPAM)) core, palladium catalytic centers, and a biobased alginate shell to enable efficient aqueous-phase reduction of nitroarene derivatives. Core–shell alginate gel beads were successfully fabricated above the lower critical solution temperature (LCST) of poly(NIPAM), yielding a structurally robust and hierarchically organized catalytic architecture. Upon thermal activation at 50 °C, the poly(NIPAM) core undergoes a reversible phase transition that generates hydrophobic domains in situ, markedly enhancing the partitioning and diffusion of hydrophobic reactants toward the embedded catalytic sites in an otherwise aqueous environment. Catalytic activity was assessed using 4-nitrophenol as a model substrate, achieving a high turnover number of 9100 and a turnover frequency of 27,324 h^{−1} at 50 °C. Moreover, the catalyst demonstrates broad substrate tolerance across both hydrophilic and hydrophobic nitroarene derivatives, while maintaining excellent physical integrity and reusability for at least five catalytic cycles. Collectively, these results underscore the significance of coupling thermoresponsive polymer physics with renewable biopolymer scaffolds to create adaptive, robust, and eco-friendly catalytic systems, offering a general strategy for sustainable catalysis under green reaction conditions.

KEYWORDS: alginate, palladium, hydrogenation, 4-nitrophenol, thermoresponsive polymers

INTRODUCTION

Smart polymers can reversibly change their physicochemical properties in response to external stimuli such as pH, temperature, or enzymatic activity.^{1,2} Among various stimuli-responsive polymers, poly(*N*-isopropylacrylamide) (PNIPAM) has attracted particular interest due to its lower critical solution temperature (LCST) of approximately 32 °C.^{3,4} Below the LCST, PNIPAM is fully soluble in water and adopts a hydrated coil conformation. In contrast, it collapses into a hydrophobic globular state above this temperature.^{5,6} This temperature-induced phase transition is reversible and tunable through copolymerization or cross-linking with other materials, enabling customizable responsiveness.

In 2023, Thirupathi et al. developed a dual pH- and temperature-responsive PNIPAM-*co*-PAAm hydrogel cross-linked with a melamine–glutaraldehyde precursor, achieving high drug-loading efficiency, controlled dual-stimuli release, and excellent biocompatibility.⁷ Similarly, PNIPAM-based systems have been combined with metal nanoparticles and other hydrogels to develop multifunctional platforms. However, the high surface energy of metal nanoparticles often leads to aggregation, resulting in instability and morphological changes.⁸ To mitigate these issues, nanoparticles are commonly immobilized on supports such as carbon, silica, zeolites, or alumina to enhance stability and reusability.^{9–12} Environmentally benign, recyclable, and cost-effective support materials are essential for improving nanoparticle durability while advancing green chemistry.¹³ Sodium alginate, a natural polysaccharide composed of β-D-mannuronic and α-L-

guluronic acid residues, can coordinate with divalent cations (e.g., Ca²⁺, Ba²⁺, and Sr²⁺) to form ionically cross-linked “egg-box” hydrogel structures.¹⁴ Owing to its excellent biocompatibility, sustainability, and ability to form hydrogels, alginate is widely utilized in drug delivery, tissue engineering, and biocatalytic systems.^{15–18}

The immobilization of metal nanoparticles within the hydrogel matrixes has been extensively explored. One of the earliest examples, reported by the Willner group, demonstrated the incorporation of gold nanoparticles (AuNPs) into polyacrylamide (PAAm) hydrogels by swelling dehydrated gels in AuNP solutions, resulting in homogeneous nanoparticle distribution.¹⁹ In 2012, Pt nanoparticles embedded in a bolaamphiphile hydrogel acted as efficient catalysts for the hydrogenation of *p*-nitroaniline.²⁰ Zhang et al. later developed PEOPPA hydrogels containing multiamine groups that enabled the in situ formation of various noble metal nanoparticles (Au, Ag, Pd, Pt, and Ru) without additional reducing or stabilizing agents, showing high activity in the NaBH₄-mediated reduction of nitroaromatics.²¹ Similarly, Pd nanoparticles supported on Fe₃O₄@SiO₂@m-SiO₂ exhibited excellent catalytic perform-

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ance in the reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol and could be magnetically recovered.²²

Among noble metals, palladium (Pd) stands out as a highly efficient hydrogenation catalyst due to its strong ability to activate molecular hydrogen and cleave C–Cl or multiple bonds. When immobilized on suitable supports, Pd catalysts show remarkable stability, selectivity, and recyclability, making them ideal for sustainable catalysis. Pd nanoparticle (PdNP)-loaded microgels, in particular, have exhibited superior catalytic activity in hydrogenation and carbon–carbon coupling reactions compared to other noble metal systems.^{23–27} Recent studies have highlighted the efficiency of Pd-microgel catalysts in the reduction of compounds such as 4-nitrophenol and rhodamine-B, as well as in situ Suzuki–Miyaura cross-coupling reactions under biological conditions to synthesize anticancer agents.^{28,29}

Gholinejad et al. optimized Pd-catalyzed nitroarene reductions using 0.1 mol % Pd loading, an EtOH–H₂O (1:1) solvent system, and NaBH₄ as a reducing agent at room temperature, achieving high to excellent yields.³⁰ In a related study, Xia et al. synthesized Ba²⁺-cross-linked alginate hydrogels loaded with Pd and Fe₂O₃ nanoparticles as recyclable catalysts for 4-nitrophenol reduction, demonstrating excellent stability and reusability.¹⁴ More recently, alginate-coated magnetic hydrogels functionalized with poly(vinylamine) (PVAm) and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) achieved a turnover frequency (TOF) of 390 h^{–1} and a rate constant of $2.95 \times 10^{-2} \text{ s}^{-1}$, further emphasizing the catalytic potential of amino-functionalized hybrid materials.³¹

The catalytic performance of the Pd-loaded PNIPAM-core/alginate-shell hybrid was systematically evaluated under various solvent conditions, including pure water, ethanol, and water/ethanol mixtures. Given that PNIPAM undergoes a thermoresponsive phase transition near 32 °C, which can significantly influence mass transfer and network permeability,³² reactions above the LCST were closely examined. The results revealed that aqueous systems provided notably higher turnover number (TON) and turnover frequency (TOF) values. This improvement was attributed to the alginate shell's ability to stabilize uniformly dispersed Pd nanoparticles and to the PNIPAM phase transition, which enhanced dispersion and prevented precipitation.^{32–35} In contrast, ethanol or mixed solvent systems exhibited relatively lower activity, consistent with previous reports on microgel- and hydrogel-supported catalysts in 4-nitrophenol reduction and Suzuki–Miyaura coupling reactions.^{7,33–36} These findings confirm that the PNIPAM–alginate hybrid hydrogel architecture provides both structural and functional advantages for water-based, eco-friendly catalytic applications.^{33–36}

In this study, a thermoresponsive poly(NIPAM) core with adjustable hydrophobic/hydrophilic properties was combined with an alginate shell to create a new hybrid catalyst system containing palladium (Pd) nanoparticles. The performance of the catalytic system was tested on the reduction of both hydrophilic and hydrophobic nitroarene derivatives in aqueous media above the LCST temperature of poly(NIPAM).

■ EXPERIMENTAL SECTION

Materials

N-Isopropylacrylamide (NIPAM, >99%) was recrystallized in *n*-hexane prior to polymerization. Palladium(II) acetate (Pd(OAc)₂,

98%), *N,N*-dimethylformamide (DMF, ACS reagent, ≥99.8%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA, powder, 97%), sodium alginate, and sodium borohydride (NaBH₄, >99%) were purchased from Sigma-Aldrich and used as received. Calcium chloride was purchased from Akkar Kimya. DMF was dried under molecular sieves 4 Å and stored under a nitrogen atmosphere. UV–vis spectra were recorded using a Thermo Fischer Evolution 201 UV–vis spectrophotometer. The morphology and elemental composition of the synthesized particles were characterized using a scanning electron microscope (SEM) with an FEI Quanta 200 FEG ESEM system. Thermogravimetric analysis (TGA) was conducted using a Thermoplus Evo TG 8120 (Rigaku Japan) device under a constant flow of nitrogen (30 mL/min) with a heating rate of 10 °C/min. Number-average molar masses (*M*_n) were determined by a size exclusion chromatography (SEC) system LC-20A from Shimadzu equipped with a SIL-20A autosampler, RID-10A, and a refractive index detector. The analysis was performed using the following column system, operating in THF (flow rate: 1.5 mL/min) at 30 °C: main-column, PSS SDV Linear XL I (300 mm × 8.0 mm). Calibration was created using narrow linear poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981 000 Da.

Synthesis of Poly(*N*-isopropylacrylamide)

N-Isopropylacrylamide (NIPAM) (0.816 g, 7.612 mmol) was dissolved in dry DMF (3 mL) at room temperature, and the solution was degassed with nitrogen for 5 min. Then, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (5 mg, 0.0304 mmol) was added to another Schlenk reactor and dissolved in 1 mL deionized water. This solution was added to the NIPAM solution, and the reactor was placed into an oil bath at 70 °C and magnetically stirred for 24 h under a nitrogen atmosphere. After that, the reaction mixture was added dropwise to cold diethyl ether to precipitate the polymer. The resulting polymer was dried at 24 °C in a vacuum oven for 48 h.

Encapsulation of Poly(NIPAM) and Pd(OAc)₂ in Calcium Alginate Gels (Pd@p(NIPAM)@Alg)

Poly(NIPAM) (0.10 g), palladium(II) acetate (25 mg), and sodium alginate (2.0 wt % aqueous solution, 5 g) were mixed in a beaker for 1 h. This solution was then added dropwise to an aqueous solution of 5 wt % CaCl₂ at 50 °C. Spherical alginate beads were formed upon contact with the solution. The alginate beads were left in the CaCl₂ solution overnight, washed with deionized water/ethanol, and then dried under high vacuum overnight. The palladium loading was determined as 0.820 mmol Pd/g (ICP-MS).

Representative Procedure for the Reduction of 4-Nitrophenol

An aqueous solution of 4-nitrophenol (0.0144 M, 10 mL) was charged to a 25 mL reactor equipped with a magnetic stirrer. Alginate beads were added, and the mixture was stirred at 200 rpm. A freshly prepared aqueous NaBH₄ solution (1 mL, 0.861 M) was added, and the reaction mixture was stirred at 50 °C. The reaction progress was monitored using a UV–vis spectrophotometer at 200–600 nm wavelengths. The conversion of 4-NP was determined by using the following equation: Conversion % = $(A_0 - A_t)/A_0 \times 100$, where *A*₀ is the initial absorption of the solution and *A*_{*t*} is the amount of absorption at given *t* time.

Representative Procedure for the Reduction of Hydrophobic Substrates (4-Nitrotoluene)

A stock solution of 4-nitrotoluene (0.010 M) was prepared in acetonitrile (10 mL). An aliquot (2.88 mL) of this solution was diluted with deionized water (47 mL) to give a 4-nitrotoluene (5.76×10^{-4} M, 20 mL) solution. This solution was charged to a 25 mL reactor equipped with a magnetic stirrer. Alginate beads were added, and the mixture was stirred at 200 rpm. A freshly prepared aqueous NaBH₄ solution (0.240 M, 500 μL) was then added, and the reaction mixture was stirred at 50 °C. UV–vis absorption spectroscopy was used to monitor the completion of reaction.

Scheme 1. Synthesis of Pd@p(NIPAM)@Alg

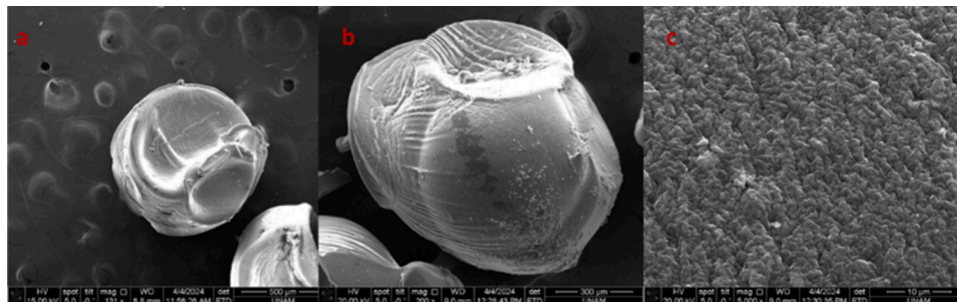
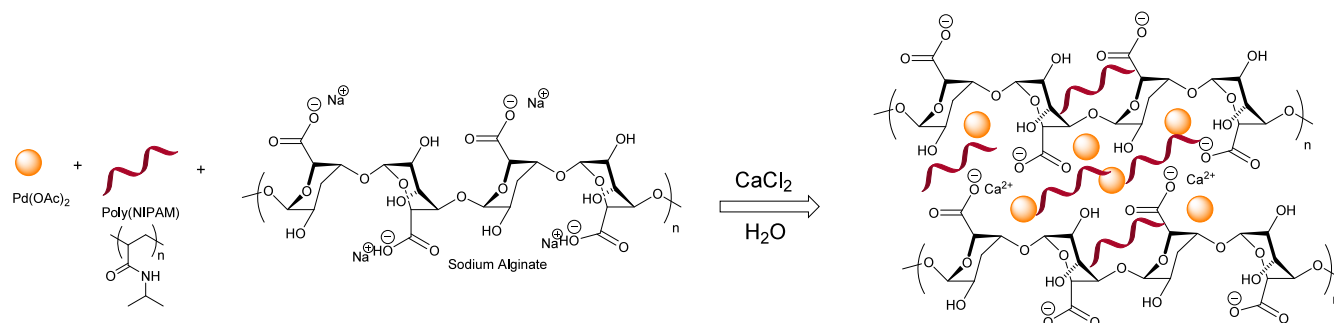


Figure 1. SEM analysis of Pd@p(NIPAM)@Alg.

Reusability Tests of Alginate Gels

An aqueous solution of 4-nitrophenol (0.0144 M, 10 mL) was charged to a 25 mL reactor equipped with a magnetic stirrer. Then, alginate beads were added to the solution, and the mixture was stirred at 200 rpm. A freshly prepared aqueous NaBH₄ solution (1 mL, 0.861 M) was added, and the reaction mixture was stirred at 50 °C. UV–vis absorption spectroscopy was used for monitoring the completion of reaction. Once the conversion of the substrate reached a plateau, the beads were taken out of the reactor with the help of a spatula, washed with ethanol (2 mL × 2)/deionized water (2 mL × 2), and used in the next cycle.

RESULTS AND DISCUSSION

Tuning the hydrophobicity of alginate gels through covalent modification and the integration of hydrophobic nano/microparticles, such as mesoporous carbon, has enhanced the catalytic performance of alginate-based catalytic systems.^{37–39} For catalytic reactions that proceed in aqueous media, the diffusion of hydrophobic reactants to active sites containing catalyst particles is of great importance. The confinement of the catalyst within hydrophobic domains may enhance mass-transport rates by optimizing the local microenvironment for the substrate.

Tunable hydrophobic/hydrophilic domains will enable the in situ formation of hydrophobic domains, thereby improving the activity and stability of the catalyst.⁴⁰ For this purpose, we have chosen poly(NIPAM) as a thermoresponsive polymer for the reversible tuning of the hydrophobic character of the catalyst core. Poly(NIPAM) was synthesized through radical polymerization reactions using 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA) as the radical initiator and DMF as the solvent (*M*_n ≈ 20,000 Da). The alginate bead synthesis protocol was optimized through varying sodium–alginate/poly(NIPAM) weight/weight (w/w) ratios, Pd(OAc)₂ and calcium chloride solution concentrations, and gel formation temperatures. In the first trial, alginate beads were formed through the dropwise addition of sodium alginate

aqueous solutions (2 wt %) to the calcium chloride (CaCl₂) solution at room temperature. Spherical or raindrop-shaped gels were formed upon contact with the calcium solution. However, these gels exhibit poor physical stability and easily lose their structural integrity in both the solution phase and the solid phase. This problem can be related to the heterogeneous encapsulation of poly(NIPAM) and Pd(II) with calcium alginate gels due to the hydrophilic character of both compounds. To construct a core–shell gel structure, we hypothesized that inducing gel precipitation above the lower critical solution temperature (LCST) of poly(NIPAM) would promote the formation of a hydrophobic poly(NIPAM) core surrounded by an alginate shell. For this purpose, we heated the aqueous CaCl₂ solution to 50 °C, which is above the LCST of poly(NIPAM) (LCST ≈ 33–34 °C), while the sodium alginate/Pd(II) solution was kept at 25 °C. The dropwise addition of the sodium alginate/poly(NIPAM) mixture at 25 °C to the CaCl₂ solution at 50 °C instantly resulted in spherical white-gel formation (Scheme 1). Upon contact with the CaCl₂ solution, alginate beads formed cross-linked structures, and the inner core appeared in white color due to the LCST transition of poly(NIPAM) to the hydrophobic phase. A semitransparent gel was formed upon cooling the resulting gels to room temperature. The gel structures showed structural stability in both the solution and solid phases and kept their structural integrity. In the next trial, the same procedure was repeated using a homogeneous mixture of palladium(II) acetate, poly(NIPAM), and sodium alginate in water at 25 °C to encapsulate metal particles within a gel structure. The obtained gels were denoted as Pd@p(NIPAM)@Alg.

The surface morphology of the Pd@p(NIPAM)@Alg beads was analyzed by means of scanning electron microscopy (SEM) (Figure 1). Alginate beads have a spherical morphology and a uniform surface. The elemental mapping of Pd@p(NIPAM)@Alg confirmed the homogeneous distribution of

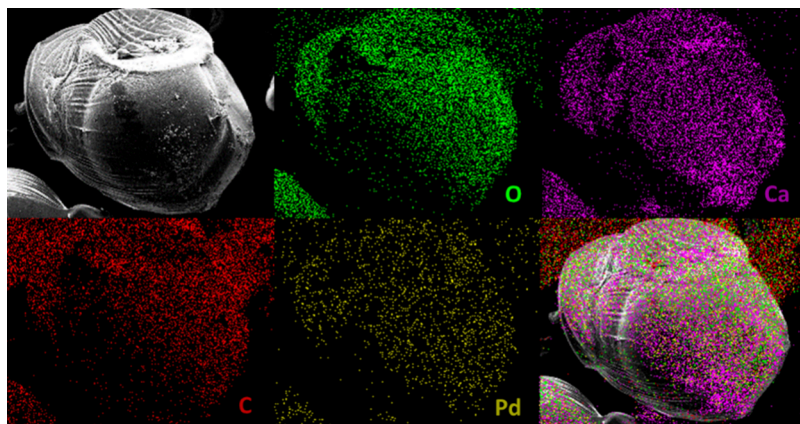


Figure 2. SEM-EDX mapping of Pd@p(NIPAM)@Alg.

Pd over the spherical alginate bead, as confirmed by SEM-EDX (energy dispersive X-ray) analysis (Figures 2 and S1, Supporting Information). The palladium loading was determined to be 0.820 mmol of Pd/g (ICP-MS).

The thermogravimetric analysis (TGA) of Pd@p(NIPAM)@Alg was carried out under nitrogen gas with a heating rate of 10 °C/min. A weight loss of 10% was observed up to 200 °C due to the loss of moisture in the gel structure. A sharp weight loss between 200 and 400 °C was associated with the decomposition of poly(NIPAM). At 900 °C, a total weight loss of 84% was observed (Figure S2, Supporting Information).

Catalytic activity tests were carried out using 4-nitrophenol (4-NP) as the test substrate and sodium borohydride (NaBH_4) as the hydrogen source. The catalytic loading (mol % Pd), NaBH_4 , and the reaction temperature were optimized. The tunable hydrophilic/hydrophobic character of the core poly(NIPAM) will allow the hydrogenation reaction to proceed smoothly above the LCST temperature. Above the LCST temperature, the hydrophobic domains will be formed within the alginate gel, which will improve the diffusion of nitroarene derivatives in aqueous media. To compare the activity of the catalyst, the reaction was carried out at both 25 and 50 °C. As can be seen in Table 1, the reaction proceeded rapidly at 50 °C, which is above the LCST temperature of poly(NIPAM) (LCST $\approx$ 34 °C), reaching complete conversion after 25 min with a catalytic loading of 9200/1 (4-NP/Pd; mol/mol). The performance difference at different temperatures (25 and 50 °C) is more evident at higher 4-NP/Pd (mol/mol) loadings (Table 1, entries 11–14). X-ray photoelectron spectroscopy (XPS) analysis of the used catalyst, Pd@p(NIPAM)@Alg, confirmed the in situ reduction of Pd (II) to Pd (0) during hydrogenation reactions, following the addition of NaBH_4 (Figure S2, Supporting Information). The brown catalyst beads were immediately transformed into black beads, also indicating the reduction of palladium (Figure S3, Supporting Information). The performance of the catalytic system under different substrate/catalyst loadings was tested, and the results are summarized in Table 1. The highest TON value of 9100 and TOF value of 27,324 h^{-1} were achieved with a catalytic loading of 9200/1. The effect of the NaBH_4 /4-NP (mol/mol) ratio on the rate of the reaction was also tested using ratios of 6/1, 10/1, and 20/1 under identical reaction conditions. It has been shown that the reaction reaches complete conversion in both cases. The reaction proceeds smoothly and rapidly in the presence of 10/1 and 20/1 NaBH_4 /4-NP (mol/mol) ratios (Table 2).

Table 1. Hydrogenation of 4-NP under Different Reaction Conditions

entry	4-NP/Pd (mol/mol) ^a	temp. (°C)	time (min)	conv. (%) ^b	TON ^c	TOF ^d (h^{-1})
1	25/1	25	1	99	25	
2		50	0.5	99	25	
3	100/1	25	1	99	99	
4		50	0.5	99	99	
5	700/1	25	10	99	693	
6		50	2	99	693	
7	1100/1	25	25	99	1090	2616
8		50	5	99	1090	13,080
9	1300/1	25	30	99	1287	2574
10		50	5	99	1287	15,444
11	3300/1	25	75	85	2805	2244
12		50	12	99	3267	16,335
13	9200/1	25	120	65	5980	2990
14		50	20	99	9100	27,300
15 ^e	9200/1	25	180	45	4140	1380
16 ^e		50	45	70	6440	8590

^aThe NaBH_4 /4-NP (mol/mol) ratio is 10/1. ^bDetermined by UV–vis spectroscopy and GC analysis reported as the average of three runs. ^cTurnover number: (mol of substrate/mol of Pd) $\times$ conversion %. ^dTurnover frequency: TON/time (h). ^e $\text{Pd}(\text{OAc})_2$ was used instead of the alginate beads.

The effect of the thermoresponsive polymer poly(*N*-isopropylacrylamide) (poly(NIPAM)) on catalytic performance was evaluated by comparing a palladium–alginate catalyst without poly(NIPAM) (Pd@Alg) and Pd@p(NIPAM)@Alg at 50 °C. The kinetics graphs were plotted over $\ln(A_t/A_0)$ versus reaction time using the $\ln\left(\frac{A_t}{A_0}\right) = -kt$ equation, where k is the kinetic constant for the specific reaction.

The hydrogenation of 4-nitrophenol (4-NP) followed first-order reaction kinetics, as confirmed in Figure 3. At 50 °C, rapid reaction rates were observed over both Pd@p(NIPAM)@Alg and Pd@Alg catalysts. Notably, the proposed hydrophobic domain effect of poly(NIPAM) appeared more pronounced in Pd@p(NIPAM)@Alg, consistent with its higher rate constant compared to Pd@Alg. The elevated rate constant ($k = 1.38 \text{ min}^{-1}$) indicates that the thermally tunable

Table 2. Effect of NaBH₄/4-NP Ratio on Reaction Performance

entry	Pd (%)	NaBH ₄ /4-NP (mol/mol)	4-NP (M)	temperature (°C)	time (min)	conv. (%) ^a
1	1	6	5.76×10^{-4}	50	5	99
2	1	10	5.76×10^{-4}	50	0.5	99
3	1	10	5.76×10^{-4}	25	1	99
4	1	20	5.76×10^{-4}	50	0.5	99

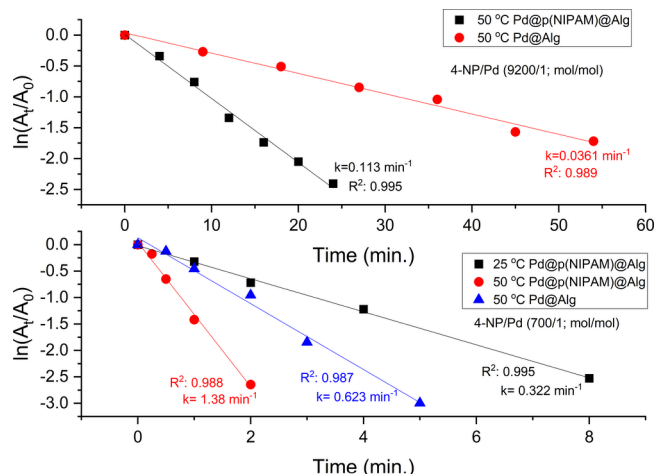
^aDetermined by UV–vis spectroscopy and GC analysis.

Figure 3. Kinetics of hydrogenation of 4-NP using different catalysts at different temperatures.

hydrophobicity of poly(NIPAM) significantly enhances the reaction rates, which is consistent with enhanced substrate–catalyst interactions. In contrast, the Pd@Alg catalyst, lacking poly(NIPAM), exhibited good mechanical durability but comparatively lower catalytic activity.

To compare the confinement effect of poly(NIPAM)/alginate, control experiments were carried out using only Pd(OAc)₂ and NaBH₄, and the results are given in Table 1,

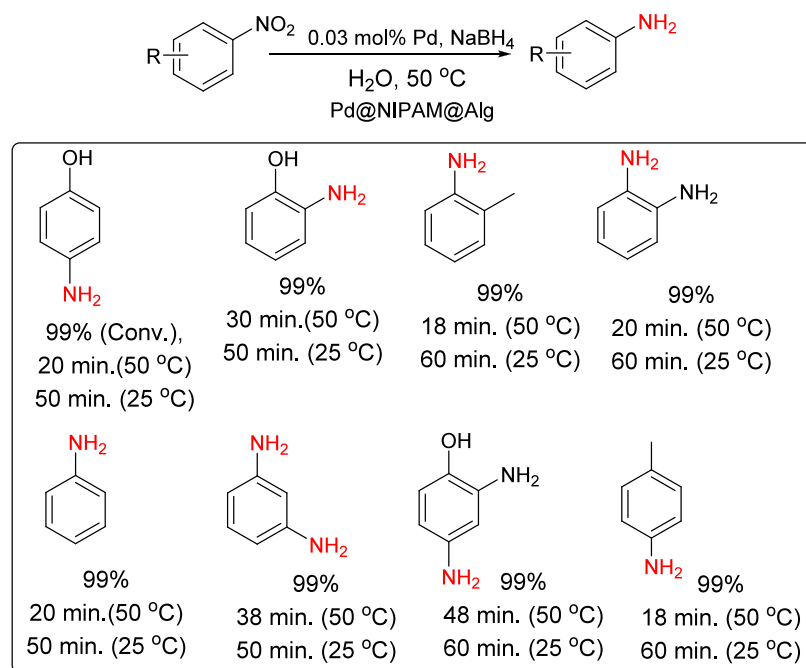
entries 15 and 16. The catalytic performance is limited due to the aggregation of nonstabilized Pd nanoparticles, resulting in significant Pd black precipitation after the reaction.

In the next trial, a variety of nitroarene derivatives, including 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 4-nitrotoluene (4-NT), 2-amino-4-nitrophenol (2A-4-NP), 2-nitroaniline (2-NA), and 2-nitrotoluene (2-NT), were tested with a catalytic loading of 3300/1 (substrate/Pd; mol/mol) at 50 °C (Scheme 2). NB, 1,3-DNB, 4-NT, and 2-NT were used as aqueous solutions containing acetonitrile at a volume ratio of 5.78%.

The reaction was carried out until substrate conversion reached a plateau. The catalytic system demonstrated high activity with both hydrophilic and hydrophobic substrates reaching quantitative conversion values (Figures S4–S9, Supporting Information). The catalyst's temperature-dependent performance underlines the specific influence of poly(NIPAM). The performance of the catalyst was also compared with other literature examples summarized in the Supporting Information section (Table S1, Supporting Information).

The reusability of the catalyst was tested with a 4-NP/Pd loading of 700/1 (mol/mol) at 50 °C under optimum reaction conditions. The Schlenk reactor was charged with Pd@p(NIPAM)@Alg and aqueous 4-NP solution. The reaction was stirred at 50 °C, and aliquots were regularly withdrawn from the reaction mixture and analyzed by UV–vis spectrophotometry. Once the conversion of 4-NP reached a plateau, the catalyst beads were separated from the reaction

Scheme 2. Hydrogenation of Various Substrates Catalyzed by Pd@p(NIPAM)@Alg



mixture, washed with ethanol/water, and taken to a fresh Schlenk reactor. As shown in Table 3, the catalyst can be

Table 3. Reusability of Pd@p(NIPAM)@Alg with a Catalytic Loading of 700/1

run ^a	1	2	3	4	5	6
conversion%	99	99	95	90	88	55
time (min) ^b	2	5	15	35	60	180

^aThe reactions were carried out with a 4-NP/Pd (mol/mol) ratio of 700/1 in the presence of 10-fold excess of NaBH₄ relative to 4-NP.

^bThis represents the time when the conversion reached a plateau.

reused up to the fifth run without significant performance loss. However, the reaction is gradually slowed down after the second run. After the fifth run, the catalyst beads retain their physical stability, and palladium leaching was measured as 5 wt %. The decreased catalytic performance during the sixth run can be attributed to multiple factors. The collapse of micro-sized gel domains within the alginate likely restricts substrate diffusion by physically blocking the active centers. Furthermore, the aggregation of Pd NPs into larger clusters reduces the available catalytic surface area. A final deactivation pathway involves the competitive chemisorption of amine derivatives onto the active Pd(0) surfaces; during repetitive runs, this resulting passivation prevents the nitroarene substrates from reaching the active sites.

Hot filtration tests were performed under optimal reaction conditions to evaluate catalyst leaching and confirm the heterogeneous nature of the process (Figure 4). The reaction

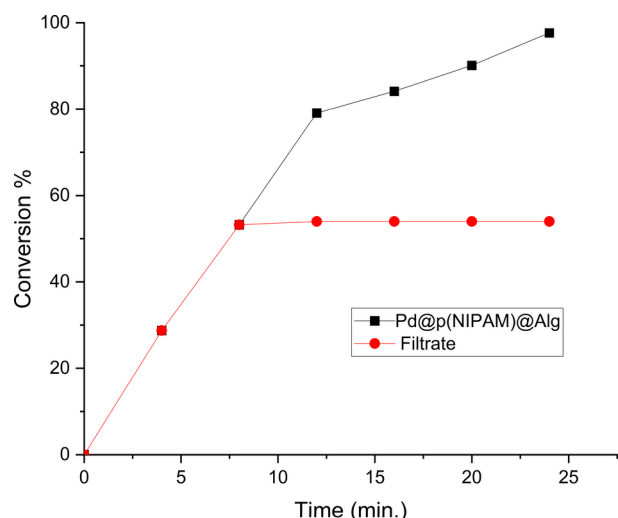


Figure 4. Hot filtration tests for the reduction of 4-NP using Pd@p(NIPAM)@Alg at 50 °C (4-NP/Pd (mol/mol): 9200/1).

was initiated at 50 °C using Pd@p(NIPAM)@Alg, 4-NP, and NaBH₄. Upon reaching 40% conversion, half of the reaction solution was filtered into a separate reactor and stirred, while the remaining half continued in the presence of the catalyst. After an additional 30 min, the 4-NP conversion in the filtrate remained unchanged, whereas the fraction containing the catalyst reached 99%. These results, further supported by ICP-MS analysis, confirm that the catalyst is truly heterogeneous and that only 0.5 wt % Pd leaching occurred during the hot filtration tests.

CONCLUSIONS

The integration of thermoresponsive polymers, specifically poly(NIPAM), into alginate gel beads has led to the formation of a more robust and effective catalytic platform for the aqueous-phase reduction of nitroarene derivatives. It is possible that operating above the LCST induces the formation of hydrophobic confinement domains within the alginate matrix, thereby facilitating the diffusion and local enrichment of hydrophobic substrates for hydrogenation reactions in water. In situ reduction of Pd(II) within the alginate network further produces a mechanically stable and catalytically efficient hybrid system capable of reducing both hydrophobic and hydrophilic nitroarene substrates. At 50 °C, the catalyst exhibits high activity at a 4-NP/Pd (mol/mol) ratio of 9,200:1, while maintaining excellent physical integrity and reusability over at least five catalytic cycles with minimal loss of performance. In contrast, operating below the LCST results in diminished catalytic efficiency, likely due to restricted network permeability and diffusion limitations. Together, these findings demonstrate that coupling smart, thermoresponsive polymers with natural polysaccharide matrices provide a powerful strategy for designing sustainable, water-based catalytic platforms. More broadly, this work highlights how thermally tunable hydrophobic–hydrophilic domains within catalyst architectures can be leveraged to reconcile the reactivity of hydrophobic substrates with eco-friendly aqueous reaction environments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.oprd.6c00065>.

XPS and TGA data for alginate beads, UV–vis spectra of nitroarene derivatives, bead particle size, and mass distribution graphs (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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