

Exploring the Potential of Calixarene-Protected Pd Nanoparticles as Effective Catalysts for Coupling Reactions: A Review

Keyur Bhatt^{1,*} , Jaymin Parikh¹ 

¹ Faculty of Science, Department of Chemistry, Ganpat University, Kherva-384012, Mehsana, Gujarat

* Correspondence: kdb01@ganpatuniversity.ac.in;

Scopus Author ID 55258010600

Received: 18.10.2023; Accepted: 7.07.2024; Published: 21.09.2024

Abstract: The incorporation of metal nanoparticles (MNPs) as catalysts has gained widespread attention recently due to their unique physicochemical properties, high catalytic activity, and selectivity in various chemical reactions. Developing efficient, low-cost, and environmentally friendly methods for synthesizing MNPs has been an active area of research. This article highlights the growing interest in calixarene-enabled metal nanoparticles (MNPs) as catalysts for various chemical reactions due to their exceptional properties, such as high catalytic activity and selectivity. The article also explores the potential applications of MNPs as catalysts in organic reactions, including reduction, oxidation, and C-C coupling reactions. Overall, this article highlights the potential of calixarene-based Pd MNPs as efficient, low-cost, and environmentally friendly catalysts for various chemical reactions and provides a platform for future research in this field.

Keywords: calixarene; catalysts; palladium nanoparticle; coupling reaction; metal nanoparticle.

© 2024 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The field of catalysis has witnessed significant growth in recent years, with metal nanoparticles (MNPs) playing a vital role in advancing various chemical transformations. These nanoparticles possess unique structural features and surface properties, making them ideal catalysts for various chemical reactions [1–3]. Despite their effectiveness, however, MNPs are prone to aggregation, limiting their stability and catalytic activity. Palladium has long been recognized as a versatile and efficient catalyst for various chemical reactions. In recent years, the development of palladium metal nanoparticles (PdNPs) has opened up new possibilities for advancing catalysis in various fields. PdNPs offer several advantages over their bulk counterparts, including a higher surface area, enhanced reactivity, and improved selectivity. Despite these benefits, PdNPs can suffer from aggregation and deactivation during catalytic reactions [4–9].

To overcome these limitations, researchers have turned to calixarene-based compounds as stabilizers for PdNPs. Calixarenes possess a unique structural feature known as the Calix platform, which allows them to bind uniformly to the surface of metal nanoparticles. The functionalization of calixarene is used to tailor the reducing ability of the stabilizer, which is crucial for synthesizing small-sized and mono-dispersed PdNPs. The parent Calix platform's vase-like skeleton also enhances the calixarene's stabilizing power, ensuring the PdNPs' stability during catalytic reactions [10,11]. Calixarene-based compounds have emerged as a

promising solution to this issue, with their ability to stabilize and enhance the performance of MNPs. Calixarenes are a family of cyclic organic molecules with a cone-like structure that enables them to bind uniformly to the surface of metal nanoparticles. By controlling the size and shape of the MNPs and modifying the functional groups of the calixarene, it is possible to tailor their catalytic properties to suit various reactions [12–14]. Recent research has focused on applying calixarene-enabled metal nanoparticles in various catalytic reactions, including hydrogenation, oxidation, and C-C coupling reactions, among others. C-C coupling reactions, in particular, have been of significant interest due to their role in synthesizing complex organic molecules. By employing MNPs stabilized with calixarenes as catalysts, these reactions can be carried out under mild conditions and with high efficiency [15–17].

Our research team has contributed significantly to the field of calixarene-enabled PdNPs, having published several studies on their synthesis, characterization, and catalytic applications. We continue to actively work towards further advancing this area of research. This review will provide a basic platform for researchers to gain insights into the latest developments in the field of calixarene-enabled PdNPs for catalytic applications, particularly in C-C coupling reactions. By examining these compounds' challenges and prospects, this review will guide researchers toward new opportunities for advancing catalysis in various fields.

2. Rationale Behind the Study

The rationale behind using Pd nanoparticles in coupling reactions lies in their exceptional catalytic properties, recyclability, environmentally friendly nature, and cost-effectiveness, making them promising catalysts for a wide range of chemical transformations [18]. The catalytic performance of PdNPs is closely linked to their intrinsic shape and size, which can be controlled to enhance their activity. Moreover, Pd NPs supported on porous organic polymers have shown excellent recyclability, maintaining their catalytic activity over multiple reaction cycles without significant decrease [19]. The development of PdNPs supported by green solvents or porous organic polymers contributes to environmentally friendly catalytic processes that align with the principles of green chemistry.

3. Synthesis Approach to Calixarene Enabled MNPs

The synthetic approach to metal nanoparticles (MNPs) encompasses diverse methods and techniques [20,21]. The interaction of MNPs with the Calix skeleton and its conformational properties have been studied. Multidentate ligands such as calixarenes have been found to be more effective in synthesizing smaller and more stable NPs than ligands with single donor groups. Multivalent calixarene ligands have also been shown to promote nucleation and protect nanoclusters from post-nuclear aggregation [22,23]. These findings can be applied to the synthetic strategy for calixarene-based PdNPs, particularly in optimizing the reduction method and the functional groups attached to the calixarene for improved catalytic performance (Figure 1).

The functionalization of calixarenes plays a significant role in preparing stable and efficient metal nanoparticles for catalytic applications. Calix systems with thiol or amine headgroups act as both surfactants and reducing agents for nanoparticles due to their polarizing and electron-donating nature, which can bring metal ions to a zero oxidation state [24,25]. The thiolated calixarene links to the surface of Au-NPs through the Au-S bond, giving more

stability to NPs, and this strong interaction is crucial for catalytic applications [26]. The stabilizing properties of functionalized Calix systems have been well described by various researchers in terms of their ability to promote the self-organization and dispersion characteristics of nanoparticles [27]. In addition, the multidentate nature of the ligands, especially those with more than one donor group, is more effective in synthesizing smaller and more stable nanoparticles, thereby enhancing their catalytic activity [28]. So, the functionalization of calixarenes is a key part of improving the catalytic qualities of MNPs, which makes them good for C-C coupling reactions and other organic transformations [29].

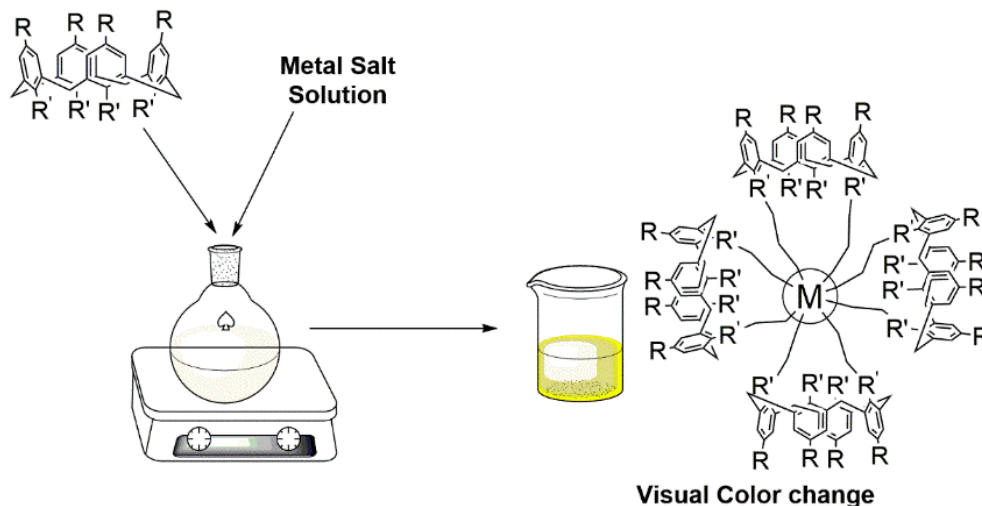


Figure 1. Common one-pot synthetic route of calixarene enabled MNPs.

Functionalized with specific groups, the calixarene moieties act as reducing and stabilizing agents for the MNPs. The calixarene moieties are usually functionalized with thiol or amine headgroups, which provide strong anchoring sites for the metal ions and also offer steric stabilization to the resulting nanoparticles. Calixarene-enabled MNPs can be synthesized using a simple, one-pot method, which involves mixing a solution of calixarene and a metal salt under gentle heating and stirring. The color change observed during the reaction is a quick indicator of the formation of nanoparticles. Further confirmation of the synthesis can be obtained through characterization techniques such as UV-Vis spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR).

4. Catalytic Applications of Calixarene-enabled PdNPs

Modi *et al.* described the strategy of thiacalixphenyl[4]arene tetra acetohydrazide (TPTAH) as a reducing and stabilizing agent for the development of palladium nanoparticles (PdNPs), which is shown to exhibit superior catalytic activity compared to conventional Pd catalyst. The incorporated molecular modeling studies to get a detailed understanding of the surface properties of TPTAH-capped PdNPs and proposed the reduction mechanism of Pd(II) to Pd(0) by hydrazide group on the tail of TPTAH [30]. TPTAH-PdNPs were characterized and found to be 4 ± 2 nm in size. These NPs are found to be catalytically active for C-C coupling reactions of Suzuki-Miyaura, Heck, and Stille reactions and were more efficient than conventional Pd catalyst yield, catalyst loading, and reaction time. They were found to be reusable for up to five reaction cycles. Table 1

Kongor *et al.* reported a novel approach to synthesizing calix[4] pyrrole-enabled PdNPs in water using calix[4]pyrrole tetrahydrazide (CPTH) [31]. The nanoparticles were

characterized and studied for their catalytic activity in the Mizoroki-Heck C-C coupling reaction. The study optimized the catalytic activity of CPTH-PdNPs for the reaction using different solvents, bases, temperatures, and amounts of catalyst. The results showed that CPTH-PdNPs were an efficient nanocatalyst with good yields and recyclability for five consecutive catalytic cycles. The study concludes that CPTH-PdNPs are an efficient and unrestrictive nanocatalyst that could be used in various organic chemical reactions.

Mehta *et al.* discuss synthesizing and characterizing a novel DHOC derivative that produces water-dispersible Pd nanoparticles (PdNps) that serve as both reducing and stabilizing agents for numerous C-C coupling reactions [32]. The optimized reaction conditions for the DHOC-PdNps catalysts were compared to conventional low-yield Pd catalysts in Suzuki, Sonogashira, and Heck reactions. The DHOC-PdNps were highly efficient in all three reactions and reusable for at least five cycles with no significant loss of effectiveness. The study suggests that DHOC-PdNps can serve as an efficient and eco-friendly catalyst for organic synthesis.

Panchal *et al.* reported a novel water-soluble tetra-methoxy resorcinarenes tetrahydrazide (TMRTH) used to entrap palladium metal to synthesize water-dispersible stable PdNPs [33]. TMRTH-PdNPs were found to be polydispersible with the size of 5 ± 2 nm, and they were found to be highly efficient in catalytic application in Suzuki-Miyaura cross-coupling reaction in comparison to conventional Pd catalysts with respect to time, catalyst loading and reusability. The optimized reaction conditions of the model reaction (solvent = 1,4-dioxane-water (1:1), base = Na_2CO_3 , temperature = 40°C , TMRTH-PdNPs loading = 0.006 mmol) were used in all Suzuki cross-coupling reactions on varying aryl halides. TMRTH-PdNPs were highly effective in reactions between various aryl halides with phenylboronic acid with a mean yield of 95 ± 1 and mean reaction time of 12 ± 2 minutes at 40°C .

In another study by Panchal *et al.*, a one-pot synthesis method was used to prepare water-dispersible palladium nanoparticles (PdNps) using oxacalix[4]arene dihydrazide (OXDH) [34]. The resulting OXDH-PdNps were characterized using various techniques and were found to be spherical with an average size of 3-4 nm and well-crystallized in a face-centered cubic structure. The OXDH-PdNps were then explored for their catalytic activity in Suzuki-Miyaura and Mizoroki-Heck coupling reactions, where they showed promising performance in terms of reaction time and yield for six consecutive cycles without significant loss in their catalytic activity.

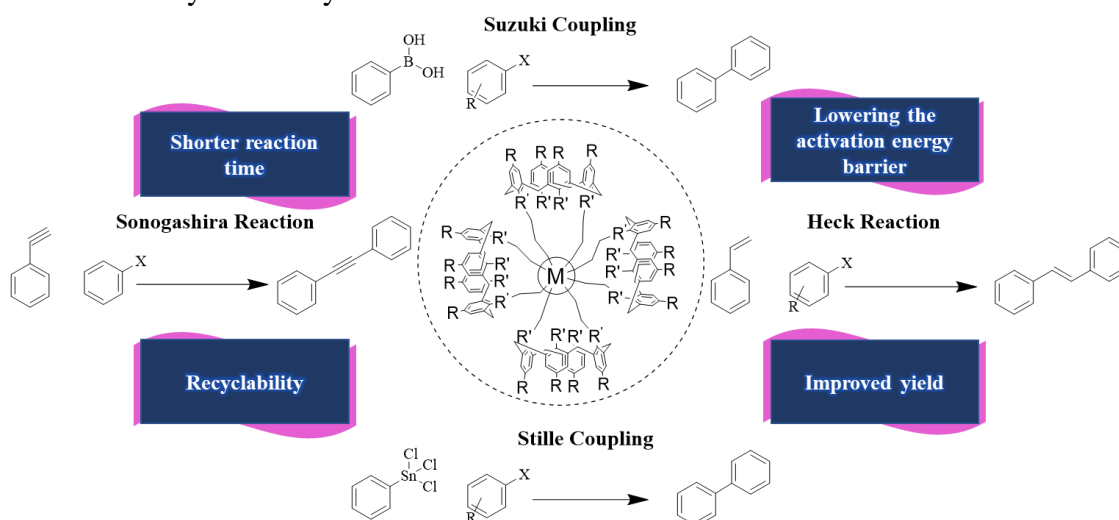


Figure 2. Calixarene enabled the PdNPs catalytic approach to different C-C coupling reactions.

The article by Desai *et al.* describes the synthesis of Pd nanoparticles using octahydrazone derivatives of calix[4]pyrroles (OHCP) as efficient and recyclable nanocatalysts for various cross-coupling reactions [35]. The stability and pH studies of the Pd nanoparticles are also discussed. OHCP is an electron-rich ligand that can reduce and encapsulate metal ions. The encapsulation of the Pd nanoparticles using OHCP enhances their activity and selectivity, making them ideal recognition partners for Pd. The article shows that OHCP-PdNPs are aqueous and air-stable and are facile and low-cost alternatives for synthesizing stable PdNPs. The catalytic activity of OHCP-PdNPs was evaluated in various C-C coupling reactions, including Suzuki, Buchwald-Hartwig, Stille, Heck, and Sonogashira reactions. They found that OHCP-PdNPs are productive catalysts for these reactions and can be reused up to five times without considerable loss in their catalytic activity.

A new type of ternary hybrid catalyst, Pd@MCM-Calixox, based on mesoporous silica, calixarene conjugate, and Pd(0) nanoparticles by Narkhede *et al.* [36]. They established calixarene's role in forming PdNPs, and NPs were shown to be an effective Suzuki coupling reaction. The hybrid catalyst shows higher activity, and they also noted that a very low concentration of Pd-based catalyst was used, and its reusability was established without any significant loss in its catalyst. The study also compared the catalytic efficiency of Pd@MCM-Calixox with that of Pd/MCM-41, which did not possess the calixarene moiety. It showed that Pd@MCM-Calixox exhibited enhanced C-C coupling activity and gave a high product yield even at low Pd content.

The study reported by Pomal *et al.* showed the use of calix[4]pyrrole tetra benzohydrazone capped Palladium nanoparticles (CPTBH-PdNPs) as a catalyst in Suzuki-Miyaura coupling reactions [37]. Spectroscopic techniques such as UV-visible, TEM, EDX, and Zeta Potential were used to characterize the nanoparticles, and they were observed to be in spherical shape with an average size of 14 ± 2 nm. They reported that these PdNPs are found to be more efficient in catalytic applications than conventional methods in Suzuki-Miyaura coupling reactions, with almost 97% yields obtained in 30 minutes with up to five cycles of catalytic applications without any loss in catalytic efficiency.

Table 1. Reaction time and yield comparison of different calixarene-enabled PdNPs catalyzed C-C coupling reactions.

Catalytic agent	TEM size	Reaction	Reaction time	Yield	Reference
thiacalixphenyl[4]arene tetra acetohydrazone-PdNPs	4 ± 2 nm	Suzuki-Miyaura	10 min	95%	[30]
		Heck	10 min	94%	
		Stille	30 h	95%	
calix[4]pyrrole tetrahydrazone-PdNPs	5-9 nm	Heck	2 h	96%	[31]
5,17-di(hydrazine carbonyl) tetranitrooxalix[4]arene-PdNPs	5 ± 2 nm	Sonogashira	20 min	92%	[32]
		Suzuki-Miyuara	60 min	90%	
		Heck	1.5 h	95%	
tetra-methoxy resorcinarene tetrahydrazone-PdNPs	5 ± 2 nm	Suzuki-Miyuara	10 min	94%	[33]
oxalix[4]arene dihydrazone-PdNPs	3-4 nm	Suzuki-Miyaura	60 min	98%	[34]
		Heck	30 min	97%	
calix[4]pyrroles octahydrazone-PdNPs	5-9 nm	Suzuki-Miyaura	15 min	94%	[35]
		Heck	15 min	93%	
		Stille	35 min	95%	
tetraallyl calixarene(MCM-allylcalix)PdNPs	12 ± 2 nm	Suzuki-Miyaura	6 h	96%	[36]

Catalytic agent	TEM size	Reaction	Reaction time	Yield	Reference
calix[4]pyrrole tetra benzohydrazide capped Palladium nanoparticles	14±2 nm	Suzuki-Miyaura	30 min	97%	[37]

5. Summary and Future Outlook

The studies discussed the synthesis and characterization of different palladium nanoparticles (PdNPs) and their application in C-C cross-coupling reactions. Common trends include the use of one-pot synthesis methods to produce MNPs with controlled size and shape, functionalization of the MNPs with various organic molecules to improve their stability and reactivity, and characterization of the MNPs using various techniques such as TEM, XRD, and FTIR. Applying MNPs as catalysts has shown promising results in various organic C-C coupling reactions (Figure 2). Future outlooks for MNPs include further development of their application in catalysis and drug delivery, as well as in other fields such as biomedicine and environmental remediation. The use of MNPs in combination with other materials, such as carbon-based materials and polymers, could also lead to the development of novel hybrid materials with improved properties. The study of the toxicity and biocompatibility of MNPs is also important for their safe application in various fields.

The use of calixarene-based Palladium (Pd) nanoparticles (NPs) as catalysts faces challenges such as difficulties in achieving stable NPs with a narrow size distribution, complex synthesis, and functionalization processes, scalability concerns for industrial applications, and the potential for Pd leaching during reactions, raising contamination worries. Overcoming these challenges is essential to maximize the effectiveness of calixarene-based Pd nanoparticles as catalysts in diverse chemical reactions.

6. Conclusions

This review highlights studies on MNP synthesis, including one-pot synthesis methods, and their applications in different catalytic reactions such as reduction, oxidation, and C-C coupling. Studies have shown that the size, shape, and surface chemistry of MNPs significantly impact their catalytic activity and selectivity. The synthesis and application of MNPs in catalysis is a promising field of research with potential applications in various fields, such as pharmaceuticals, materials science, and energy. Future research in this area should focus on developing more efficient and sustainable methods for synthesizing MNPs, improving their stability and reusability, and exploring their potential applications in new fields.

Funding

This research received no external funding.

Acknowledgments

The authors are thankful to CARS-GUNI, Ganpat University, Mehsana, for providing library facilities and support for research work.

Conflicts of Interest

The authors declare no conflict of interest

References

1. MubarakAli, D.; Kim, H.; Venkatesh, P.S.; Kim, J.-W.; Lee, S.-Y. A Systemic Review on the Synthesis, Characterization, and Applications of Palladium Nanoparticles in Biomedicine. *Appl. Biochem. Biotechnol.* **2023**, *195*, 3699–3718, <https://doi.org/10.1007/s12010-022-03840-9>.
2. Chandio, A.A.; Memon, S.; Memon, A.A.; Balouch, A.; Memon, R.; Thebo, K.H.; Memon, F.N.; Agheem, M.H.; Memon, S.S.; Otho, A.A. Eco-Friendly Conversion of *p*-Nitrophenol into *p*-Aminophenol Using Calix[4]arene Derived CuO Nanoparticles: An Excellent Catalytic Agent. *Polycyclic Aromat. Compd.* **2023**, *43*, 4843–4855, <https://doi.org/10.1080/10406638.2022.2096648>.
3. Song, Y.; Xiao, Y.; Pei, W.-Y.; Zhang, J.-Y.; Liu, C.; Ma, J.-F. A Calix[4]resorcinarene-Copper(II) Based Supramolecular Nanocapsule with Encapsulated Polyoxometalates for Enhanced Photocatalytic Activity. *ACS Appl. Nano Mater.* **2023**, *6*, 11902–11911, <https://doi.org/10.1021/acsanm.3c01760>.
4. Khalily, M.A.; Ustahuseyin, O.; Garifullin, R.; Genc, R.; Guler, M.O. A supramolecular peptide nanofiber templated Pd nanocatalyst for efficient Suzuki coupling reactions under aqueous conditions. *Chem. Commun.* **2012**, *48*, 11358–11360, <https://doi.org/10.1039/c2cc36228g>.
5. Fihri, A.; Bouhrara, M.; Nekoueshahraki, B.; Basset, J.-M.; Polshettiwar, V. Nanocatalysts for Suzuki cross-coupling reactions. *Chem. Soc. Rev.* **2011**, *40*, 5181–5203, <https://doi.org/10.1039/c1cs15079k>.
6. Mohammadi, M.; Ghorbani-Choghamarani, A. L-Methionine–Pd complex supported on hercynite as a highly efficient and reusable nanocatalyst for c–c cross-coupling reactions. *New J. Chem.* **2020**, *44*, 2919–2929, <https://doi.org/10.1039/C9NJ05325E>.
7. Bhattacharya, S.; Barba-Bon, A.; Zewdie, T.A.; Müller, A.B.; Nisar, T.; Chmielnicka, A.; Rutkowska, I.A.; Schürmann, C.J.; Wagner, V.; Kuhnert, N.; Kulesza, P.J.; Nau, W.M.; Kortz, U. Discrete, Cationic Palladium(II)-Oxo Clusters via f-Metal Ion Incorporation and their Macrocyclic Host-Guest Interactions with Sulfonatocalixarenes. *Angew. Chem. Int. Ed.* **2022**, *61*, e202203114, <https://doi.org/10.1002/anie.202203114>.
8. Khormi, A.Y.; Al-Shehri, B.M.; Al-Zahrani, F.A.M.; Hamdy, M.S.; Fouda, A.; Shaaban, M.R. Palladium Nanoparticles Incorporated Fumed Silica as an Efficient Catalyst for Nitroarenes Reduction via Thermal and Microwave Heating. *Catalysts* **2023**, *13*, 445, <https://doi.org/10.3390/catal13020445>.
9. Sabadasch, V.; Dachwitz, S.; Hannappel, Y.; Hellweg, T.; Sewald, N. Acrylamide-Based Pd-Nanoparticle Carriers as Smart Catalysts for the Suzuki–Miyaura Cross-Coupling of Amino Acids. *Synthesis* **2022**, *54*, 3180–3192, <https://doi.org/10.1055/a-1782-4224>.
10. Hussain, I.; Capricho, J.; Yawer, M.A. Synthesis of Biaryls via Ligand-Free Suzuki–Miyaura Cross-Coupling Reactions: A Review of Homogeneous and Heterogeneous Catalytic Developments. *Adv. Synth. Catal.* **2016**, *358*, 3320–3349, <https://doi.org/10.1002/adsc.201600354>.
11. Pomal, N.; Patel, N.; Parikh, J.; Bhatt, K.D. Strapped Calix[4]Pyrrole: Emerging Trends Based on Calix Protected Metal Nanoparticles. In Proceedings of the Tailored Functional Materials, Mukherjee, K., Layek, R.K., De, D., Eds.; Springer, Singapore, **2022**; Volume 15, 457–466, https://doi.org/10.1007/978-981-19-2572-6_34.
12. Wei, A. Calixarene-encapsulated nanoparticles: self-assembly into functional nanomaterials. *Chem. Commun.* **2006**, 1581–1591, <https://doi.org/10.1039/b515806k>.
13. Kongor, A.R.; Mehta, V.A.; Modi, K.M.; Panchal, M.K.; Dey, S.A.; Panchal, U.S.; Jain, V.K. Calix-Based Nanoparticles: A Review. *Top Curr. Chem.* **2016**, *374*, 28, <https://doi.org/10.1007/s41061-016-0029-z>.
14. Mazinani, A.; Zare, K.; Moradi, O.; Attar, H. Sulfonated calixarene modified Poly(methyl methacrylate) nanoparticles: A promising adsorbent for Removal of Vanadium Ions from aqueous media. *Chemosphere* **2022**, *299*, 134459, <https://doi.org/10.1016/j.chemosphere.2022.134459>.
15. Shalaeva, Y.V.; Morozova, J.E.; Gubaidullin, A.T.; Saifina, A.F.; Shumatbaeva, A.M.; Nizameev, I.R.; Kadirov, M.K.; Ovsyannikov, A.S.; Antipin, I.S. Photocatalytic properties of supramolecular nanoassociates based on gold and platinum nanoparticles, capped by amphiphilic calix[4]resorcinarenes, towards organic dyes. *Colloids Surf. A: Physicochem. Eng. Asp.* **2020**, *596*, 124700, <https://doi.org/10.1016/j.colsurfa.2020.124700>.
16. Yang, X.; Xu, Q. Encapsulating Metal Nanocatalysts within Porous Organic Hosts. *Trends Chem.* **2020**, *2*, 214–226, <https://doi.org/10.1016/j.trechm.2019.12.001>.
17. Kongor, A.; Panchal, M.; Athar, M.; Vora, M.; Makwana, B.; Jha, P.C.; Jain, V. Calix[4]pyrrole Stabilized PdNPs as an Efficient Heterogeneous Catalyst for Enhanced Degradation of Water-Soluble Carcinogenic Azo Dyes. *Catal. Lett.* **2021**, *151*, 548–558, <https://doi.org/10.1007/s10562-020-03304-x>.

18. Zadmand, R.; Hokmabadi, F.; Jalali, M.R.; Akbarzadeh, A. Recent progress to construct calixarene-based polymers using covalent bonds: synthesis and applications. *RSC Adv.* **2020**, *10*, 32690-32722, <https://doi.org/10.1039/D0RA05707J>.
19. Shi, G.; Dong, Z. Palladium Supported on Porous Organic Polymer as Heterogeneous and Recyclable Catalyst for Cross Coupling Reaction. *Molecules* **2022**, *27*, 4777, <https://doi.org/10.3390/molecules27154777>.
20. Kaur, M.; Gautam, A.; Guleria, P.; Singh, K.; Kumar, V. Green synthesis of metal nanoparticles and their environmental applications. *Curr. Opin. Environ. Sci. Health* **2022**, *29*, 100390, <https://doi.org/10.1016/j.coesh.2022.100390>.
21. Bordiwala, R.V. Green synthesis and Applications of Metal Nanoparticles.- A Review Article. *Results Chem.* **2023**, *5*, 100832, <https://doi.org/10.1016/j.rechem.2023.100832>.
22. Chen, Z.; Liu, J.; Evans, A.J.; Alberch, L.; Wei, A. Calixarene-Mediated Synthesis of Cobalt Nanoparticles: An Accretion Model for Separate Control over Nucleation and Growth. *Chem. Mater.* **2014**, *26*, 941–950, <https://doi.org/10.1021/cm402484x>.
23. Ha, J.-M.; Katz, A.; Drapailo, A.B.; Kalchenko, V.I. Mercaptocalixarene-Capped Gold Nanoparticles via Postsynthetic Modification and Direct Synthesis: Effect of Calixarene Cavity-Metal Interactions. *J. Phys. Chem. C* **2009**, *113*, 1137–1142, <https://doi.org/10.1021/jp808165f>.
24. de Silva, N.; Ha, J.-M.; Solovyov, A.; Nigra, M.M.; Ogino, I.; Yeh, S.W.; Durkin, K.A.; Katz, A. A bioinspired approach for controlling accessibility in calix[4]arene-bound metal cluster catalysts. *Nat. Chem.* **2010**, *2*, 1062-1068, <https://doi.org/10.1038/nchem.860>.
25. Makwana, B.A.; Vyas, D.J.; Bhatt, K.D.; Darji, S.; Jain, V.K. Novel fluorescent silver nanoparticles: sensitive and selective turn off sensor for cadmium ions. *Appl. Nanosci.* **2016**, *6*, 555-566, <https://doi.org/10.1007/s13204-015-0459-x>.
26. Patel, G.; Menon, S. Recognition of lysine, arginine and histidine by novel p-sulfonatocalix[4]arene thiol functionalized gold nanoparticles in aqueous solution. *Chem. Commun.* **2009**, 3563-3565, <https://doi.org/10.1039/b905141d>.
27. Sachdeva, G.; Bamal, Y.; Ladan, A.; Tiwari, O.S.; Rawat, V.; Yadav, P.; Verma, V.P. Calixarene-Metal Complexes in Lactide Polymerization: The Story so Far. *ACS Omega* **2023**, *8*, 13479-13491, <https://doi.org/10.1021/acsomega.2c08028>.
28. Mouarrawis, V.; Plessius, R.; van der Vlugt, J.I.; Reek, J.N.H. Confinement Effects in Catalysis Using Well-Defined Materials and Cages. *Front. Chem.* **2018**, *6*, 419863, <https://doi.org/10.3389/fchem.2018.00623>.
29. Maity, D.; Gupta, R.; Gunupuru, R.; Srivastava, D.N.; Paul, P. Calix[4]arene functionalized gold nanoparticles: Application in colorimetric and electrochemical sensing of cobalt ion in organic and aqueous medium. *Sens. Actuators B: Chem.* **2014**, *191*, 757-764, <https://doi.org/10.1016/j.snb.2013.10.066>.
30. Modi, K.; Patel, C.; Panchal, U.; Liska, A.; Kongor, A.; Jiri, L.; Jain, V.K. Facile construction & modeling of a highly active thiacalixphenyl[4]arene-protected nano-palladium catalyst for various C–C cross-coupling reactions. *New J. Chem.* **2019**, *43*, 5611-5622, <https://doi.org/10.1039/C8NJ05866K>.
31. Kongor, A.; Panchal, M.; Mehta, V.; Bhatt, K.; Bhagat, D.; Tipre, D.; Jain, V.K. Basketing nanopalladium into calix[4]pyrrole as an efficient catalyst for Mizoroki-Heck reaction. *Arab. J. Chem.* **2017**, *10*, 1125-1135, <https://doi.org/10.1016/j.arabjc.2016.06.019>.
32. Mehta, V.; Panchal, M.; Kongor, A.; Panchal, U.; Jain, V.K. Synthesis of Water-Dispersible Pd Nanoparticles Using a Novel Oxacalixarene Derivative and their Catalytic Application in C–C Coupling Reactions. *Catal. Lett.* **2016**, *146*, 1581-1590, <https://doi.org/10.1007/s10562-016-1781-y>.
33. Panchal, U.; Modi, K.; Panchal, M.; Mehta, V.; Jain, V.K. Catalytic activity of recyclable resorcinarene-protected antibacterial Pd nanoparticles in C-C coupling reactions. *Chin. J. Catal.* **2016**, *37*, 250-257, [https://doi.org/10.1016/S1872-2067\(15\)61021-X](https://doi.org/10.1016/S1872-2067(15)61021-X).
34. Panchal, M.; Kongor, A.; Mehta, V.; Vora, M.; Bhatt, K.; Jain, V. Heck-type olefination and Suzuki coupling reactions using highly efficient oxacalix[4]arene wrapped nanopalladium catalyst. *J. Saudi Chem. Soc.* **2018**, *22*, 558-568, <https://doi.org/10.1016/j.jscs.2017.09.006>.
35. Bhatt, K.D.; Desai, A.; Modi, K.; Kongor, A. Coupling Reactions by Highly Efficient Octacalix[4] Pyrrole Wrapped Scrupulous Nano-Palladium Catalyst. *Biointerface Res. Appl. Chem.* **2021**, *11*, 7632–7645, <https://doi.org/10.33263/BRIAC111.76327645>.
36. Narkhede, N.; Uttam, B.; Rao, C.P. Calixarene-Assisted Pd Nanoparticles in Organic Transformations: Synthesis, Characterization, and Catalytic Applications in Water for C–C Coupling and for the Reduction

- of Nitroaromatics and Organic Dyes. *ACS Omega* **2019**, *4*, 4908–4917, <https://doi.org/10.1021/acsomega.9b00095>.
37. Pomal, N.C.; Bhatt, K.D.; Patel, A.S.; Dholariya, M.P.; Kundariya, D.S.; Parikh, J. From catalysis to combat: calix[4]pyrrole-wreathed palladium nanoparticles as ambidextrous tools against cancer and tuberculosis. *Appl. Nanosci.* **2024**, *14*, 161-176, <https://doi.org/10.1007/s13204-023-02970-8>.