DESIGN OF HETEROGENEOUS COBALT NANOCATALYSTS STABILIZED BY NATURAL EUTECTIC SOLVENTS FOR APPLICATIONS IN ORGANIC SYNTHESIS

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Abstract

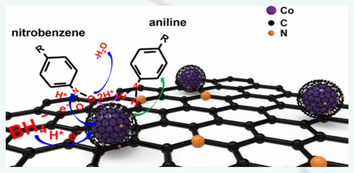
Catalysis plays an essential role in the synthesis of organic compounds, fully aligning with the ninth principle of sustainable chemistry. In recent years, nanomaterials have emerged as promising catalysts, offering stability, recyclability, and high efficiency. Among the most widely used catalysts in organic synthesis are those derived from palladium (Pd), a highly effective but costly and scarce metal. As a result, the development of more abundant and affordable alternatives, such as cobalt (Co), has garnered significant attention.[1] Co nanocatalysts not only overcome the economic and availability limitations of Pd but also introduce unique properties, such as magnetic behavior, which facilitates catalyst recovery and reuse. Additionally, the reduction of nitro compounds remains a pivotal reaction for obtaining amine derivatives, compounds of critical importance in both the chemical and pharmaceutical industries.[1] Herein, we present the synthesis and stabilization of Co nanoparticles (Co NPs) in natural eutectic solvents (NADEs) and evaluate their catalytic performance in the reduction of nitro compounds. Depending on their composition, NADEs demonstrated stabilizing properties for the synthesis of Co nanocatalysts, providing a greener and more efficient approach that enhances the sustainability of catalytic processes.

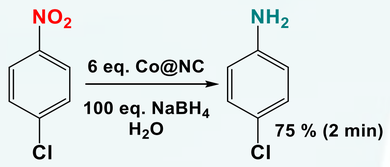
1. *Formenti, O. et al. Chem. Rev.* ***2019****, 119,* 2611−2680

Goals

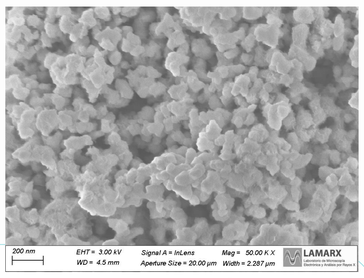
- Prepare colloidal Co nanocatalysts through the chemical reduction of Co^{2+} salts in NADEs as solvent and stabilizing media
- Assess the potential of eutectic solvents as stabilizers for Co nanocatalysts
- Evaluate the catalytic activity of Co nanocatalysts in the reduction reactions of nitro compounds, employing as a model *p*-chloronitrobenzene

Background



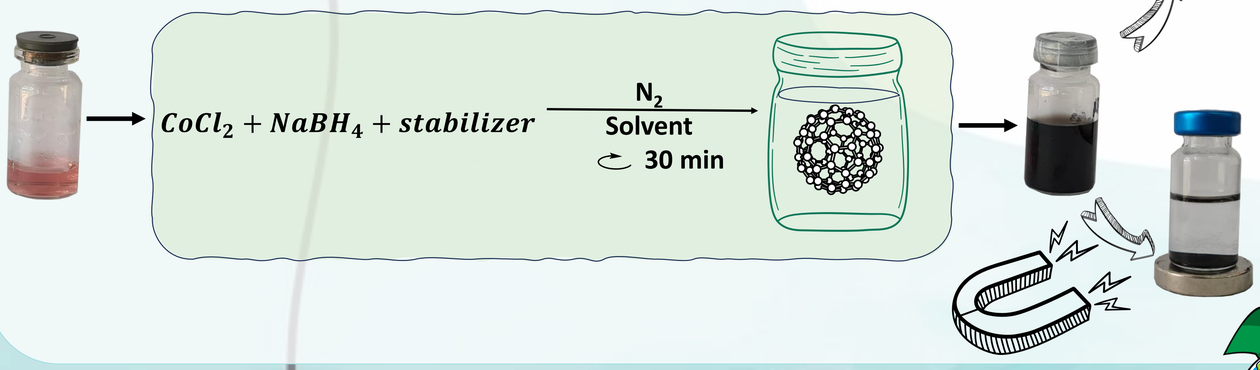


Xu, Y. *et al. Ind. Eng. Chem. Res.* **2020**, *59, 10,* 4367–4376

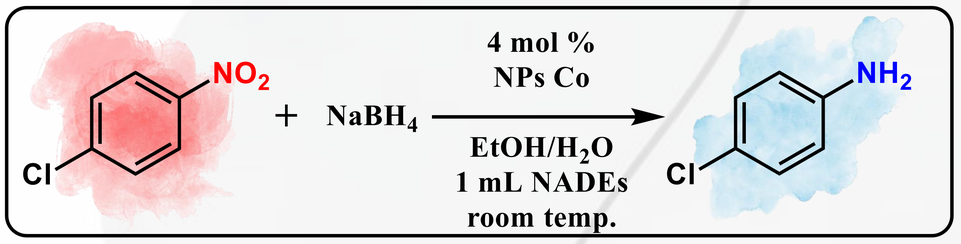


GuaHCl:1,3-PDOH

NPs Co synthesis



Catalytic activity in reduction of nitrocompounds



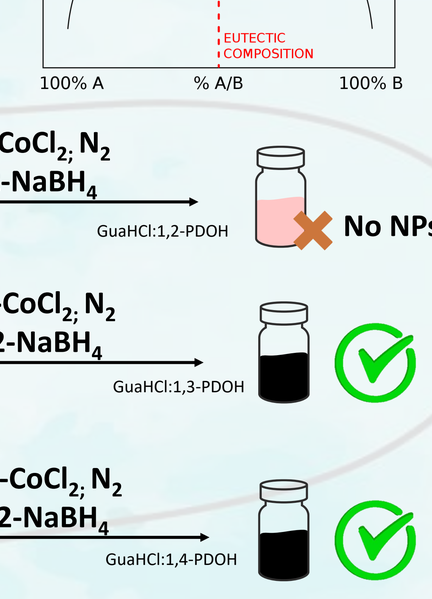
NADES	Amine (%)
ChCl:Gly*	--
ChCl:Gly:H_2O*	52%
GuaHCl:1,2-PDOH	--
GuaHCl:1,3-PDOH	**99%**
GuaHCl: 1,4-BDOH	81%
GuaHCl: DEG	28 %

*ChCl:Gly: Choline Chlorhydrate + Glycine (common NADEs)

NADEs as reaction media and stabilizer for Co NPs

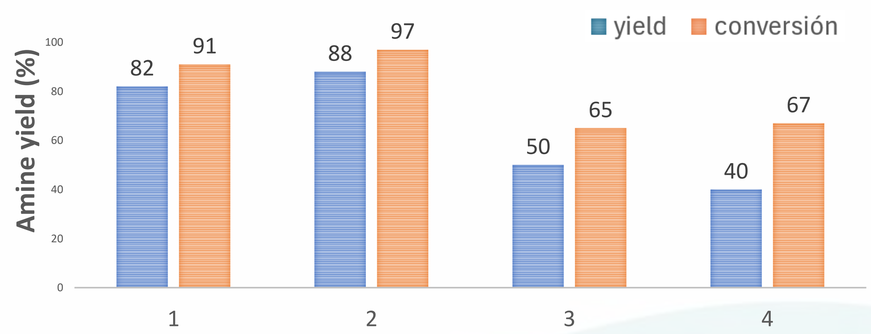
NADEs (Natural Deep Eutectic Solvents) are formed by mixing natural compounds that, when combined, reach the eutectic point of the solution at a specific eutectic temperature.[2]

2. Długosz, O. Materials ***2023****, 16, 627*



NADEs

Recycling experiments



NADEs: GuaHCl:1,3-PDOH

Conclusions

- Co NPs were successfully prepared in NADEs using $NaBH_4$ as the reducing agent. It was observed that N_2 atmosphere is essential for maintaining the stability of the colloidal dispersion.
- NADES have proven to be promising **solvents** and **stabilizing** agents for storing Co NPs, with the obtained NPs remaining stable and reactive even after 3 months of preparation.
- Nanoparticles synthesized in NADES showed excellent catalytic activity in the reduction of nitrocompounds under mild conditions and can be recycled up to the 4th cycle.
- Using NADES as solvents probe to be useful when stabilizing the Co NPs and protecting this NPs from O_2, avoiding their oxidation.

Acknowledgements and Fundings