

A STUDY OF DIFFERENT COMPOUNDS AS EFFICIENT MAGNETICALLY RETRIEVABLE AND RECOVERABLE NANOCATALYSTS FOR MULTI-COMPONENT SYNTHESIS

VINOD MEHTA, DR. KAUSHAL KUMAR SAXENA

DESIGNATION- RESEARCH SCHOLAR SUNRISE UNIVERSITY ALWAR
DESIGNATION- ASSISTANT PROFESSOR SCHOLAR SUNRISE UNIVERSITY
ALWAR

ABSTRACT

The yields, selectivity, and scalability of the green synthetic approaches were compared to standard techniques in comparative studies. The outcomes prove that our green methods work, showing that sustainable operations don't have to sacrifice either the environment or the bottom line. Our research might have far-reaching consequences for organic synthesis, and we highlight the need to embrace sustainable practices if we are to keep up with the increasing demand for ecologically friendly chemical reactions. A more environmentally friendly and sustainable future in the field of heterocyclic chemical synthesis is being actively pursued, and our study adds to that endeavor. By integrating these technologies into standard operations, we may lessen the chemical industry's impact on the environment and speed up the discovery of useful molecules with a wide range of potential uses.

KEYWORDS: Magnetically Retrievable, Recoverable Nano catalysts, Multi-Component Synthesis, chemical reactions, organic synthesis, heterocyclic chemical synthesis.

INTRODUCTION

With their many uses in areas as diverse as heterogeneous catalysis, biotechnology/biomedicine, data storage, magnetic fluids, MRI, and magnetic resonance imaging, magnetic nanoparticles (MNPs) are an essential component of today's scientific and technological landscape.¹⁻³ For organic synthesis, MNPs have shown promise as catalyst supports or sustainable catalysts owing to their exceptional characteristics, such as their large surface area, lack of toxicity, recoverability using an external magnet, and ability to evade catalytic processing and filtering.^{4, 5} The biomedical and catalytic fields have made more use of the functionalized MNPs.⁶⁻⁸ To investigate their catalytic potential for different organic

conversions, MNPs have been supported with a number of metal NPs or metal complexes, such as palladium, gold, ruthenium, copper, rhodium, vanadium, and manganese.⁹⁻²⁰

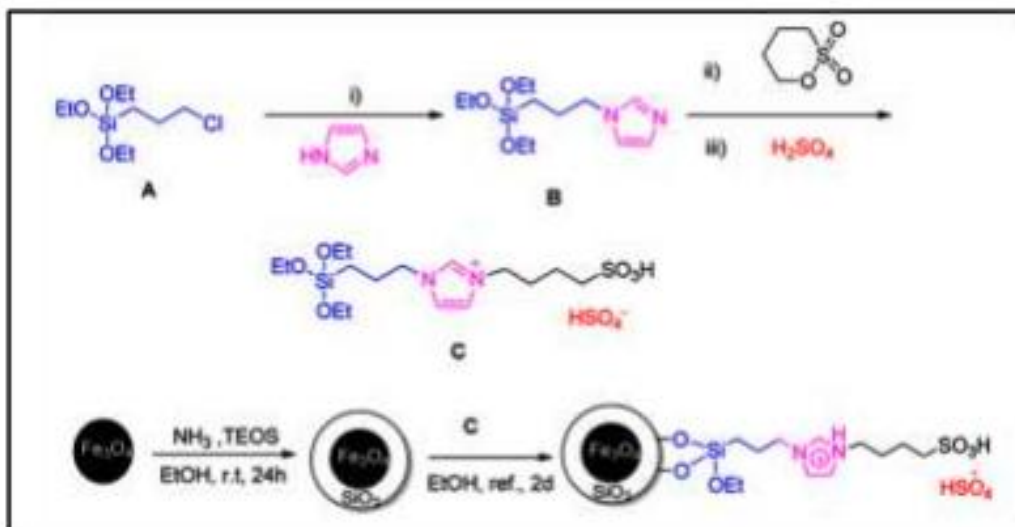
For the carbonylative Sonogashira coupling process that does not include phosphine, Xia et al. (2008) looked at the possibility of using Pd(0) supported Fe₃O₄ NPs as magnetically recoverable nanocatalysts.⁹ As a hybrid organic-inorganic nanocatalyst for the Suzuki-Miyaura cross-coupling process, Thiel et. al. (2010) studied palladium (II)-phosphine complexes supported γ -Fe₂O₃ NPs.¹⁰ Despite the many benefits of MNPs, there were a number of stages involved in preparing the phosphine-based complex, which is known as the (L)₂PdCl₂/SiO₂@Fe₂O₃. A study conducted by Luo et. al. has shown that catalysts for the Suzuki-Miyaura cross-coupling reaction may be effectively facilitated by phosphine-free palladium supported SiO₂@Fe₃O₄.^{Eleven} Yin et al. looked at the possibility of using hierarchical assemblies of magnetite-cored silica colloids as new supports for stabilizing Au(0) NPs. In the presence of NaBH₄, these hierarchical assemblies that may be recovered magnetically were discovered to be effective catalysts for the reduction of 4-nitrophenol.

By immobilizing Au³⁺ on the surface of silica-coated ferrite NPs and then reducing the metal, Rossi et al. (2010) described the synthesis of Au(0)/SiO₂@Fe₃O₄ NPs. Exploring the potential of magnetically recoverable Au(0)/SiO₂@Fe₃O₄ NPs catalysts for aerobic benzyl alcohol oxidation was their area of investigation.

By first in situ generating Fe₃O₄@SiO₂ and then immobilizing Ru NPs, Varma et al. demonstrated the gram scale synthesis of Ru supported silica coated Fe₃O₄. An effective and recyclable nanocatalyst for reducing carbonyls to alcohols was discovered in the Ru/SiO₂@Fe₃O₄. The hydration of nitriles to amides in an aqueous media was also reported for the [Ru(OH)]_x supported on dopamine functionalized ferrite.

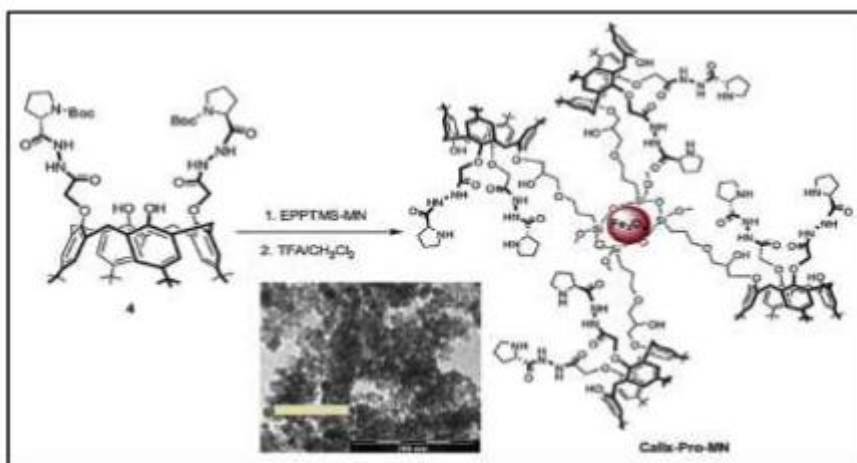
Approaches for functionalization of MNPs K-Nezhad and coworkers approach

The production of acidic ionic liquid grafted SiO₂ coated Fe₃O₄, as illustrated in Scheme 1, was published by K-Nezhad et. al. in 2015. Under moderate reaction conditions, the MNPs were discovered to be an effective catalyst for the one-pot synthesis of new spirooxindole derivatives.



Scheme 1: Schematic representation for the preparation of IL/SiO₂@Fe₃O₄ NPs

The method used by Yilmaz et al. A recent study by Yilmaz et. al. discovered that calixarene-proline functionalized Fe₃O₄ NPs (Calix-Pro-MN) may effectively facilitate the asymmetric aldol reaction in water using magnetically recoverable catalysts (Scheme 2). Aldol products were produced in high yields with outstanding stereoselectivity when aromatic aldehydes and cyclohexanone were reacting with a Calix-Pro-MN catalyst.

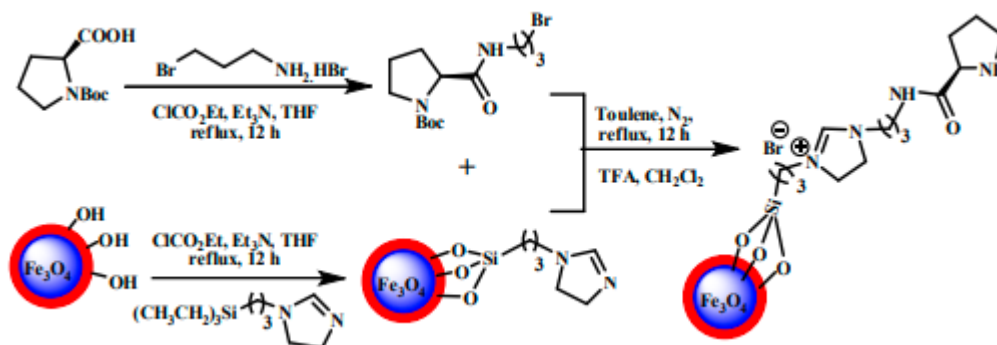


Scheme 2: Preparation of calixarene-proline functionalized Fe₃O₄ NPs

Tan and co-workers approach

Recyclable nanocatalysts for the direct asymmetric aldol reaction were described by Tan et. al. as L-proline supported imidazolium functionalized Fe₃O₄ NPs (Scheme 3). We used a

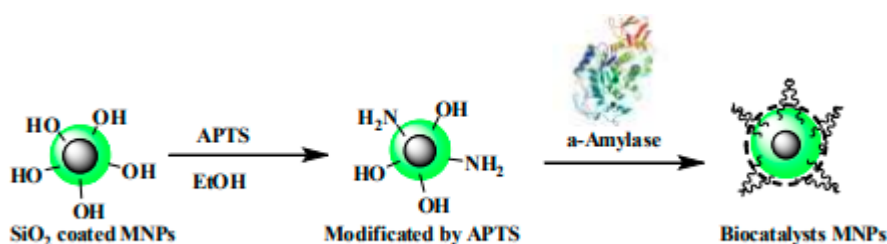
battery of characterisation methods to learn about the functionalized Fe₃O₄ core's L-proline moiety. The product was obtained with high enantioselectivity and diastereoselectivity by a reaction of cyclohexanone with 2-nitrobenzaldehyde with a catalyst present at a concentration of 10 mol%. With little to no activity loss, the catalyst was able to be retrieved from the reaction liquid using an external magnet and reused.



Scheme 3: Schematic representation for the synthesis of proline functionalized MNPs

Zhang and co-workers approach

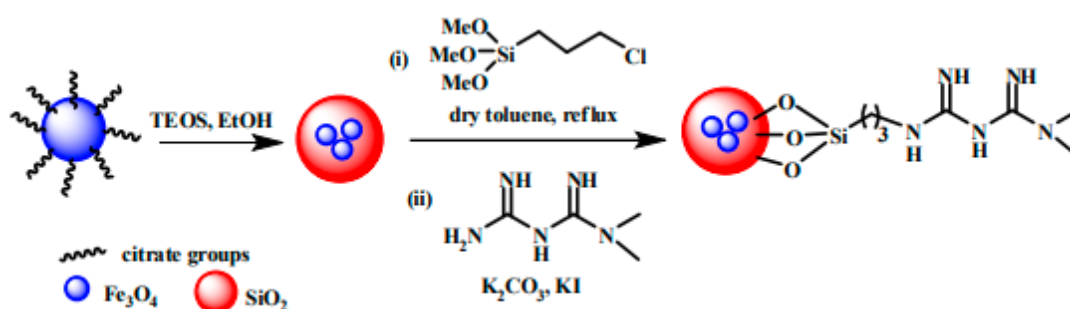
In Scheme 4, Zhang et. al. demonstrated the possible use of α -amylase functionalized APTS/SiO₂/Fe₃O₄ NPs as a biocatalyst that may be recovered by magnetic fields. The immobilized α -amylase was made more stable by improving the aggregation of Fe₃O₄ NPs in solution, which was achieved by covering them with silica. The thermal stability and reusability of this catalyst would demonstrate various uses, and this technology might be beneficial for industrial scale manufacture of biocatalyst at cheap cost.



Scheme 4: Schematic representation for the preparation of magnetic biocatalysts

Alizadeh and co-workers approach

Using a simple technique, as shown in Scheme 5, Alizadeh et al. discovered biguanide-functionalized silica coated Fe₃O₄ NPs. Magnetically recoverable nanocatalyst for nitroaldol and domino Knoevenagel condensation/Michael addition/cyclization processes in aqueous media were discovered to be the biguanide/SiO₂@Fe₃O₄ NPs.



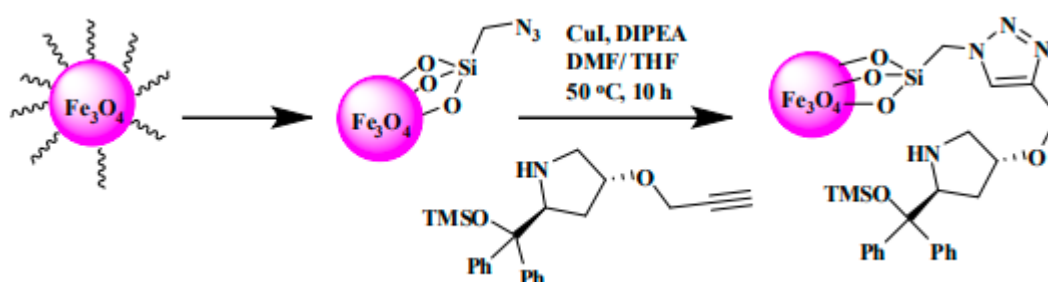
Scheme 5: Schematic representation for the synthesis of biguanide/SiO₂@Fe₃O₄ NPs

Pericas and co-workers approach

The procedure indicated in the scheme was used by Pericas et. al. to graft an alkyne derivative based on (S)- α,α -diphenyl prolinol onto azide functionalized Fe₃O₄ NPs using a Cu catalyzed click process.

The prepared (S)- α,α -diphenyl prolinol@Fe₃O₄ NPs was found to be efficient

product with excellent enantioselectivity, facilitated by a reusable catalyst for an asymmetric Michael addition process.



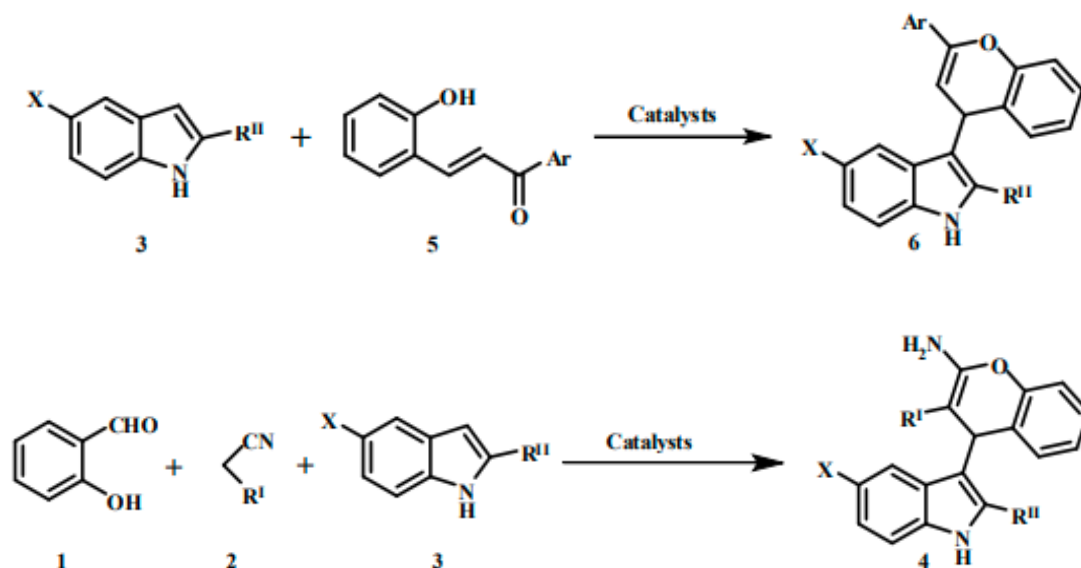
Scheme 6: Synthesis of (S)- α,α -diphenyl prolinol supported MNPs

Significance of 2-amino-4-(indol-3-yl)-4H-chromenes

Anticancer, antibacterial, antidyslipidemic, antidepressant, antitrypanosomal, anti-AIDS, monoamine oxidase (MAO) inhibitor, and numerous other pharmacological activities are exhibited by 4H-chromenes, an important class of O-heterocyclic compounds found in both plants and animals. Significant classes of N-heterocycles, indoles are present in complex natural products and exhibit a wide range of pharmacological effects.

Particularly noteworthy among these 3-substituted indoles are their impressive biological activities, which include inhibiting cell proliferation of human colon carcinoma (HT-29), inhibiting nonsteroidal aromatase against breast cancer (SK-OV-3), and acting as an HIV-1 integrase inhibitor and antiviral agent against HSV-1.48 2-(indol-3-yl)- (4-amino) In order to achieve two distinct biological effects, hybrid compounds like -4H-chromenes combine two different pharmacophores, such as indoles and 4H-chromenes.

As far as we are aware, no study has documented the biological assessment of indolyl-4H-chromene hybrids. But as you'll see below, there aren't many techniques for creating these hybrids. The one-pot synthesis of indolyl-4H-chromene was documented by Perumal et. al. in 2007 (Scheme 7). It included reacting salicylaldehydes with active methylene compounds and indoles while using InCl_3 as a catalyst.



Scheme 7: One-pot three component synthesis of 2-amino-4-(indol-3-yl)-4H-chromenes

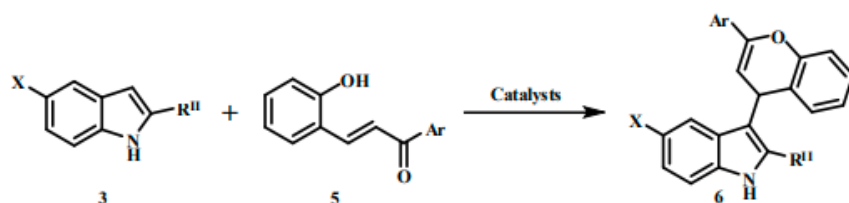
It was after this that Feng et al. looked into the enantioselective one-pot synthesis of 2-amino-4-(indol-3-yl)-4H-chromenes with a catalyst of $\text{N,N}'$ -dioxide- Zn(II) .⁵⁰ To synthesize indolyl-

4H-chromene, Ganguly et al. (2012) used L-proline as an organocatalyst in a water-based solution including an anionic surfactant like sodium dodecyl sulfate (SDS).

The possibility of using TBAF52 as a catalyst for the synthesis of 2-amino-4-(indol-3-yl)-4H-chromenes was studied by Singh et. al. in 2013 and by Das et. al. in 2014, separately (Scheme 7).

Scheme 8.54 shows the reaction between 2-hydroxychalcone and indole in the presence of a catalytic quantity of iodine, which Yin et. al. (2012) formulated as a technique for the synthesis of 2-aryl-4-(indol-3-yl)-4H-chromenes. A Michael addition and intramolecular cyclization are the steps that lead to the products in the domino reaction.

Amberlyst-15, a sulfonated polystyrene resin, has recently been mentioned by Mallik et al. as a possible recyclable heterogeneous catalyst for the 2-aryl-4-(indol-3-yl)-4H-chromenes synthesis.



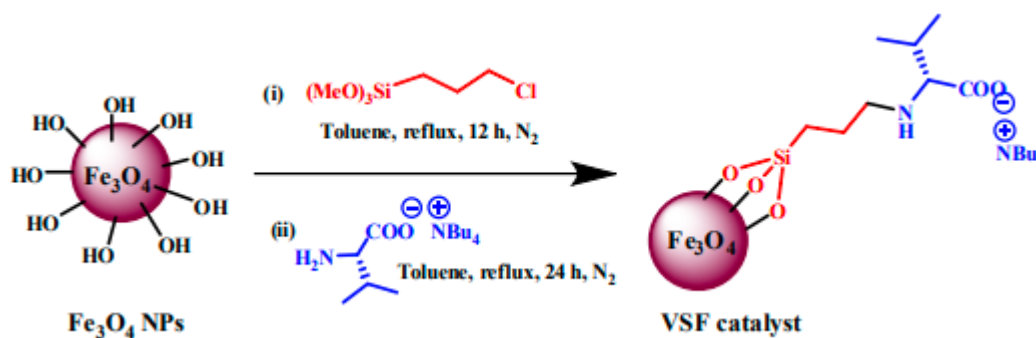
Scheme 8: One-pot two component synthesis of 2-aryl-4-(indol-3-yl)-4H-chromenes

The one-pot synthesis of 2-amino-4-(indol-3-yl)-4H-chromenes employing MNPs as recyclable nanocatalysts has not been reported, however. We investigated functionalized Fe₃O₄ NPs in this chapter as potential new magnetically recoverable nanocatalysts for 2-amino-4-(indol-3-yl)-4H-chromene production.

Synthesis and characterization of tetrabutylammonium valinate functionalized Fe₃O₄ NPs

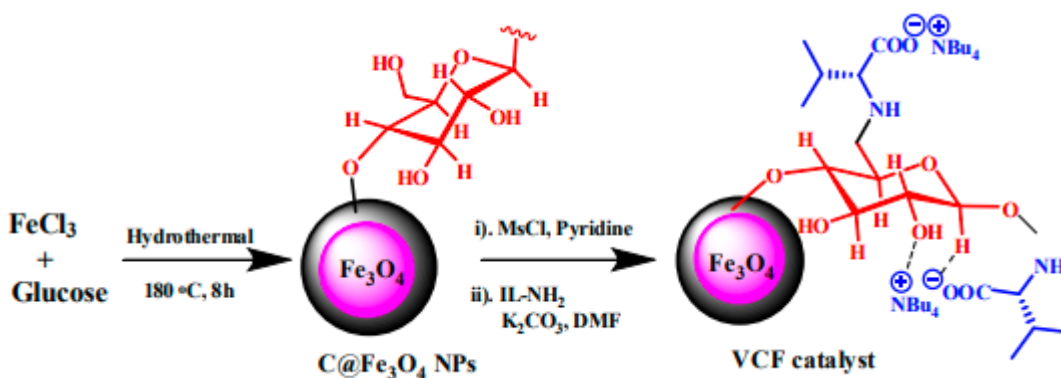
Two distinct approaches were used to graft tetrabutylammonium valinate ionic liquid (VIL) onto functionalized Fe₃O₄ nanoparticles (NPs). Based on Scheme 9, the first method produced VSF, or VIL grafted silane functionalized ferrite, by functionalizing Fe₃O₄ NPs with 3-chloropropyltriethoxysilane reagent and then grafting [NBu₄][Val] ionic liquid (VIL) in the presence of K₂CO₃. Functionalizing Fe₃O₄ NPs with a hazardous reagent like 3-

chloropropyltriethoxysilane goes against the ideals of green chemistry. As seen in Scheme 10, we devised an alternate procedure to address the issue with the previous one by substituting carbon coated Fe₃O₄ for the silane functionalized ferrite.



Scheme 9: Schematic representation for the synthesis of VSF nanocatalyst

Hydrothermal synthesis of FeCl₃ and glucose at 180 °C was used to produce carbon-coated Fe₃O₄ nanoparticles (C@Fe₃O₄). Surface functional groups, such as primary hydroxyls, are present on the produced C@Fe₃O₄ NPs. The main hydroxyl groups were mesylated at room temperature with the help of the reagent methanesulfonyl chloride in the presence of pyridine. A straightforward conventional heating process was used to graft the NH₂ group of VIL onto the mesylated hydroxyl groups of C@Fe₃O₄ NPs, resulting in the VCF catalyst (Scheme 10).



Scheme 10: Schematic representation for the synthesis of VCF nanocatalyst

Thermal gravimetric analysis (TGA & DTG), scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and vibrating sample magnetometer (VSM) were among the methods used to characterize the VSF and VCF nanocatalysts that were synthesized.

CONCLUSION

Through the A3 coupling reaction, we were able to create a new and effective Cu/HM catalyst that could be used in a one-pot synthesis of several pyrrolo[1,2-a]quinolines from quinoline-2-carboxaldehyde, phenyl acetylenes, and secondary amines. The solvent had a significant impact on the selectivity of pyrrolo[1,2-a]quinoline or chalcone synthesis. To our surprise, we were able to produce a 2-quinolinyl propargyl amine intermediate when HM was present as a scaffold. We postulated that the strong catalytic activity of Cu/HM is a result of the complementary effects of Cu^{2+} and Mg^{2+} on the HM support. There are a number of ways in which the current catalytic system excels over previously reported methods. These include adhering to green chemistry criteria, which include a smaller E-factor, PMI, and higher AE, RME, as well as recovering and reusing the Cu/HM catalyst and DEG solvent five times without losing catalytic activity. In a one-pot Wittig reaction in water, we were able to synthesize E-selective α,β -unsaturated esters using hydromagnesite, a new and efficient base catalyst. Environmental friendliness, moderate reaction conditions, convenience of handling, strong E-selectivity, outstanding yields, and facile catalyst removal from reaction mixture are only a few of the benefits of this approach. It is also broadly applicable for olefination of diverse aldehydes. The recyclability of catalysts is a downside, however. The discovery that C@Nq is a reusable catalyst for a one-pot Wittig reaction in water is very intriguing. The production of propargylamines via the A3 coupling reaction was also facilitated by HM, which was discovered to be an effective recyclable catalyst. Lewis acidic site Mg^{2+} and Bronsted basic sites such as hydroxides (-OH) and bicarbonates (HCO_3^-) for activating the acetylenic bond were responsible for HM's catalytic activity in the A3 coupling process. In comparison to previously reported methods, the current catalytic system offers several benefits, such as a transition metal free approach that results in a higher product yield in a shorter reaction time, the ability to recover and reuse the HM catalyst up to five times without a decrease in catalytic activity, and compliance with green chemistry criteria, such as a smaller E-factor, PMI, and higher AE, RME.

REFERENCES

1. Teir, Sebastian & Eloneva, Sanni & Fogelholm, Carl-Johan & Zevenhoven, Ron. (2009). Fixation of carbon dioxide by producing hydromagnesite from serpentinite. Applied Energy. 86. 214-218. 10.1016/j.apenergy.2008.03.013.

2. Ummadisetti, Rajesh & Pavan, Satya & Rawat, Diwan. (2015). Hydromagnesite Rectangular Thin Sheets as Efficient Heterogeneous Catalysts for the Synthesis of 3-Substituted Indoles via Yonemitsu-Type Condensation in Water. *ACS Sustainable Chemistry & Engineering*. 3. 1536–1543. 10.1021/acssuschemeng.5b00236.
3. Wu, Xiaoming & Cao, Huaqiang & Yin, Gui & Yin, Jiefu & Lu, Yuexiang & li, Baojun. (2010). MgCO₃·3H₂O and MgO complex nanostructures: Controllable biomimetic fabrication and physical chemical properties. *Physical chemistry chemical physics : PCCP*. 13. 5047-52. 10.1039/c0cp01271h.
4. Hopkinson, Laurence & Kristova, Petra & Rutt, Ken & Cressey, Gordon. (2012). Phase transitions in the system MgO–CO₂–H₂O during CO₂ degassing of Mg-bearing solutions. *Geochimica Et Cosmochimica Acta - GEOCHIM COSMOCHIM ACTA*. 76. 10.1016/j.gca.2011.10.023.
5. Li, Jia & Luo, Mingzhi & Wang, Kun & Li, Gaomiao & Zhang, Guoquan. (2023). Review of carbon dioxide mineralization of magnesium-containing materials. *Carbon Neutralization*. 2. 10.1002/cnl2.80.
6. Bai, Peng & Sharratt, Paul & Yeo, Tze & Bu, Jie. (2011). Production of Nanostructured Magnesium Carbonates from Serpentine: Implication for Flame Retardant Application. *Journal of Nanoengineering and Nanomanufacturing*. 1. 272-279. 10.1166/jnan.2011.1030.
7. Ma, Li & Zhang, Xiaoyue & Lin, Dan & Chun, Yuan & Xu, Qinhua. (2013). Preparation of shaped magnesium oxide/carbon catalysts using rice grains as an exotemplate and carbon precursor. *Applied Catalysis A: General*. s 460–461. 26–35. 10.1016/j.apcata.2013.04.018.
8. Botha, Alma & Strydom, Christien. (2003). DTA and FT-IR analysis of the rehydration of basic magnesium carbonate. *Journal of Thermal Analysis and Calorimetry*. 71. 987-996. 10.1023/A:1023355016208.
9. Selvamani, T. & Sinhamahapatra, Apurba & Bhattacharjya, Dhrubajyoti & Mukhopadhyay, Indrajit. (2011). Rectangular MgO microsheets with strong catalytic activity. *Materials Chemistry and Physics*. 129. 853 - 861. 10.1016/j.matchemphys.2011.05.055.



10. Künzel, Carsten & Zhang, F. & Ferrándiz-Mas, Veronica & Cheeseman, C.R. & Gartner, Ellis. (2017). The mechanism of hydration of MgO-hydromagnesite blends. *Cement and Concrete Research*. 103. 10.1016/j.cemconres.2017.10.003.
11. Fernández, Ana & Chimenos, Josep & Segarra, Mercè & Fernández, Miguel & Espiell, Ferran. (2000). Procedure to Obtain Hydromagnesite from a MgO-Containing Residue. *Kinetic Study. Industrial and Engineering Chemistry Research*. 39. 3653-3658. 10.1021/ie0003180.
12. Chintareddy, Venkat & lakshmi Kantam, Mannepalli. (2011). Recent Developments on Catalytic Applications of NanoCrystalline Magnesium Oxide. *Catalysis Surveys From Asia - CATAL SURV ASIA*. 15. 89-110. 10.1007/s10563-011-9113-0.