Chapter - 2

Application of Zeolite-based Nanocomposites

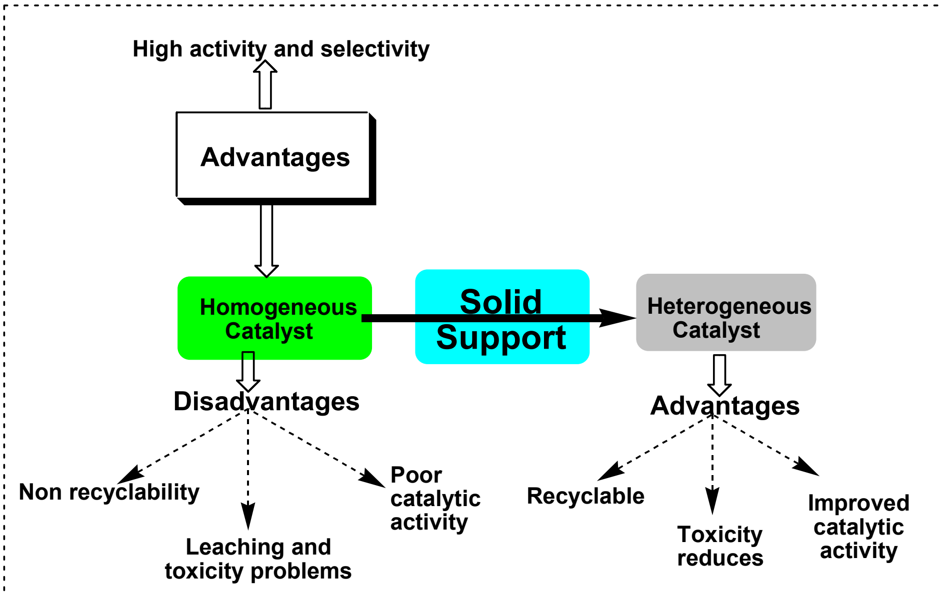
Mukesh Sharma, Mitu Sharma and Biraj Das

Department of Chemical Sciences,
Tezpur University 784028,
Assam, India

Abstract—*This chapter will discuss the various applications of metal-based zeolite nanocomposites in different organic transformations. Special emphasis has been given towards the Suzuki-Miyaura Cross-Coupling reaction with zeolite-based nanocomposites. Zeolites are highly applicable as heterogeneous support due to their high thermal stability and surface area. The prime importance of zeolite lies in its ability to trap different active species inside the nano-dimensioned cages..*

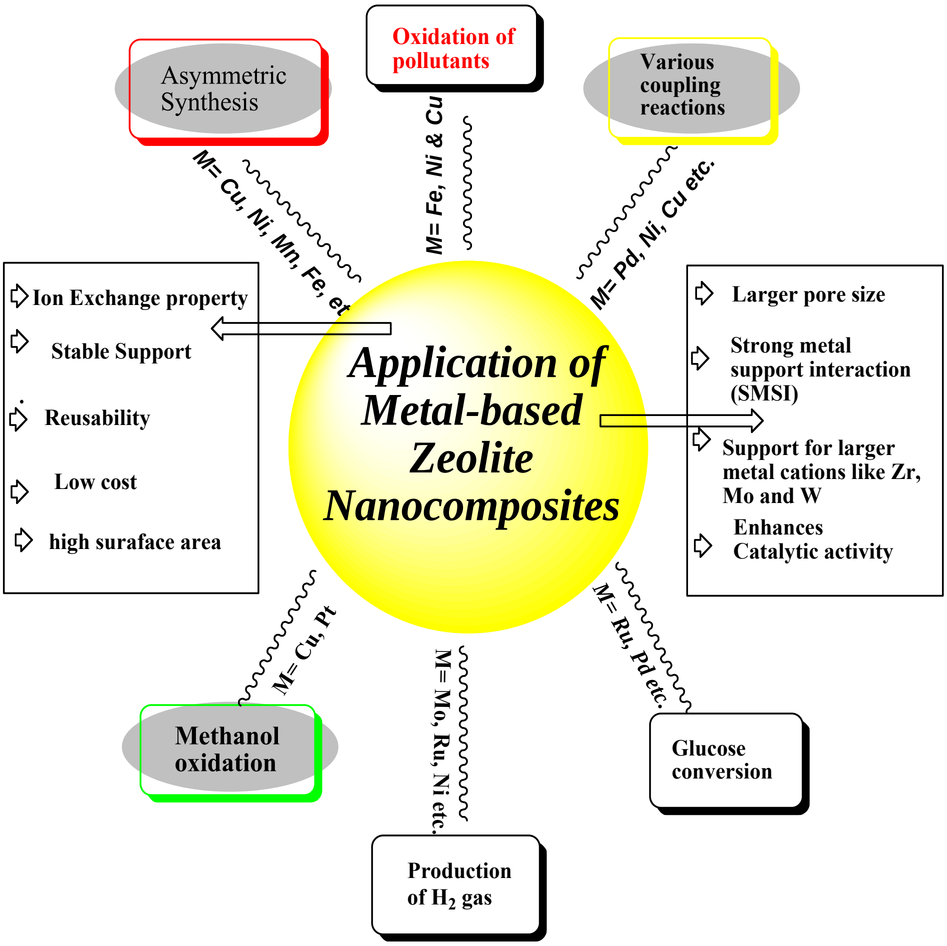
Introduction

Apart from having several advantages of homogeneous catalysts, nowadays its applicability in various fields of catalysis are losing attention due to many drawbacks like leaching of transition metal ions from the metal catalysts, non-recyclability and in most of the cases, there is a huge loss in catalytic activity.[1] Because of such defects with homogeneous catalysis, a huge emphasis has been made out for the heterogenization of active homogeneous catalyst. Heterogenization technique has now become one of the most successful techniques for many researchers because of its advantages like easy recyclability, lesser toxicity, and better catalytic activity (Scheme 1). Recently, several researchers have developed many advanced techniques to heterogenize transition metal catalyst.[1] Ion exchanged, immobilization and encapsulation onto inorganic support are some of the well-known methods used for the designing of a solid heterogeneous catalyst.[1,2] One of such approach is on different materials like metal oxides, MWCNT's, zeolite-Y, graphene oxide, etc. Among the various supports, zeolites-Y are well recognised in the synthesis of various transition metal-based catalyst and are also used in many petrochemical industries for cracking, hydrogenation purpose and in various organic transformations.[2-5]



Scheme 1. Homogeneous vs. heterogeneous catalyst, their advantages, and disadvantages.

ISBN: 978-93-85822-94-0

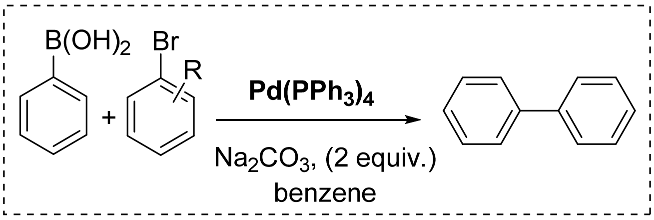


Application of Zeolite in Suzuki Reaction

Suzuki-Miyaura Cross-Coupling Reaction

Suzuki-Miyaura cross-coupling reaction, also known by the name Suzuki coupling reaction is a trailblazing reaction in C-C bond formation. In 1981 Suzuki and Miyaura published the first Suzuki type cross-coupling reaction between phenylboronic acid and haloarenes as shown in Scheme 2. The reaction after this has emerged into a field of continuous research.[6]

ISBN: 978-93-85822-94-0



Scheme 2. Suzuki-Miyaura cross-coupling reaction.

The mechanism of the reaction was not reported then.

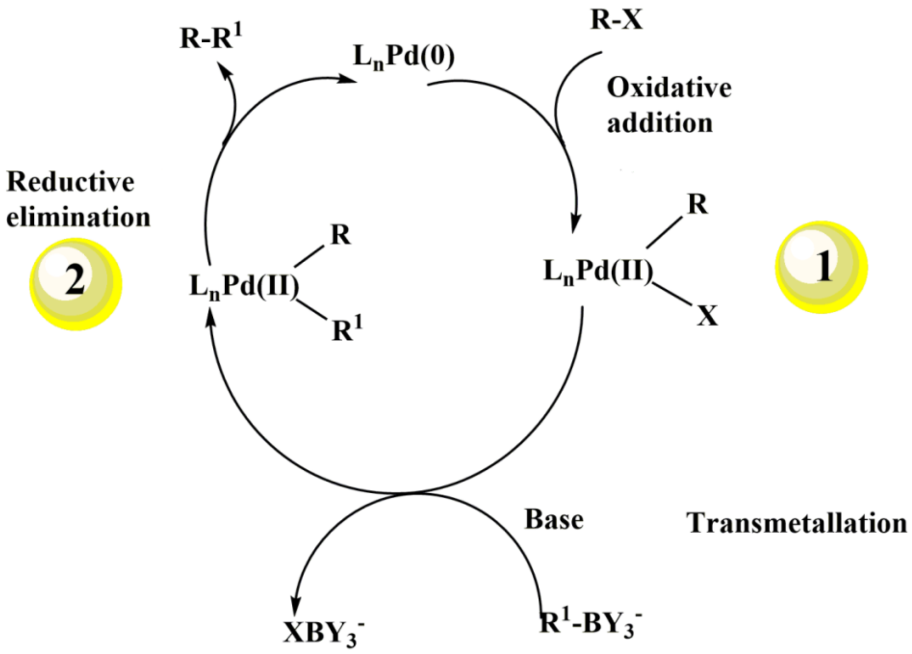
Mechanism. It was not until 1995 when Norio Miyaura and Akira Suzuki proposed their cross-coupling reaction mechanism. The general catalytic cycle for Suzuki cross-coupling reaction has been depicted in Scheme 3, and it involves three fundamental steps[7], namely,

1. Oxidative Addition: This is the first step in the Suzuki-Miyaura cross-coupling reaction, and in most cases, these are the rate-determining steps.[7] In this step, the Pd-based catalysts are oxidized from Pd (0) to Pd (II) and result in the breaking of the carbon-halogen bond. This leads to a situation where the aryl halide (R-X) group after dissociation to R and X gets attached to the oxidized Pd (II) catalyst, as shown in Scheme 3.

2. Transmetallation: This is the second step where there is a transfer of ligand from the organoboron species to form the organopalladium species. In many cases, the exact role of base is not properly defined whereas it is supposed that the base has an influential role in activating the organoboron compound as well as accelerates the transmetallation step. Recently, several groups found that the support too play a vital role in the transmetallation process.

ISBN: 978-93-85822-94-0

3. Reductive Elimination: This is the last step in the coupling process where the biphenyl product gets eliminated from the Pd(II) complex and also regenerates the active Pd(0) species.



Scheme 3. General catalytic cycle for Suzuki-cross-coupling reaction.

The oxidative addition of aryl halides to the active catalyst, Pd(0) complex leads to intermediate 1, a Pd(II) species. Under the presence of a base, an organoborane compound forms a tetra-coordinated anion, which reacts with intermediate 1 in transmetallation to form intermediate 2. This step is then followed by reductive elimination to give the desired product and regenerate the active catalyst, the Pd(0) complex in the first step. Each of the steps shown above involves further tricky processes like ligand exchanges, but there is no doubt regarding the presence of intermediates

ISBN: 978-93-85822-94-0

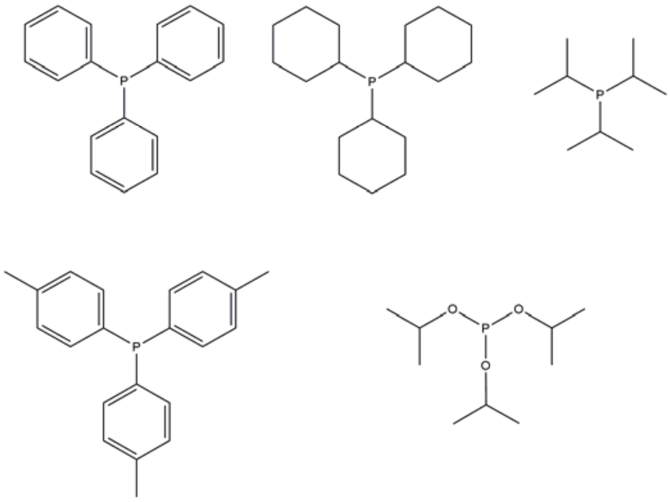
(1 and 2) which has been characterized by isolation and spectroscopic analysis.[8]

Importance of Catalyst Design

Suzuki coupling reactions most widely employs palladium catalysts, and the active Pd catalyst consists of two parts: precursors (like $Pd(OAc)_2$ and $Pd(PPh_3)_4$), and ligands. The catalysts were developed to be electron-rich and spatially bulky, to enhance the reactivity and stability of the catalyst, which affords a high turnover number (TON) and low loading. Further, palladacycles were developed which exhibited thermal stability, robust reaction times, insensitivity to air and water, low cost, and was found to be environmentally friendly.[9,10] In pharmaceutical and industrial synthesis, polymer-supported heterogeneous catalysts have a huge impact, due to the advantage of preventing contamination from ligand residue in products, easy recyclability of catalyst and its fast recovery.[9,10]

Importance of Ligand design

Ligands were designed with electron-rich and spatially bulky features keeping in mind that electron-rich ligands could assist the oxidative addition step, and spatially bulky structures boost the orbital overlapping on the metal which facilitates the reductive elimination. The earliest ligand employed in Suzuki reactions were triphenylphosphine (PPh_3). After this, researchers used different substituents on the phosphorus atom and aromatic ring to tune the reactivity. For example, Fu and other research groups substituted aromatic groups with more electron-rich and bulkier alkyl groups (Scheme 4). This led to high catalytic reactivity on less reactive substrates with lower catalyst loading.[11]



Scheme 4. Different bulky ligands employed for catalyst preparation.

Suzuki-Miyaura Coupling Reaction with Ligand system

Herein, we briefly discuss the catalysts based on palladium that utilizes phosphanes, Schiff bases, and N-heterocyclic carbenes as ligands. Also, nickel-based systems have been reported using N-heterocyclic carbene. Similarly, various palladium complexes were also immobilized on different insoluble supports like silica, MCM-41, zeolites, alumina, carbon, hydrotalcites, etc. However, out of the various supports silicon-based inorganic mantles like zeolite-Y has been extensively used as a great heterogeneous support not only in Suzuki reactions but also has wide applicability in many other organic transformations.[12]

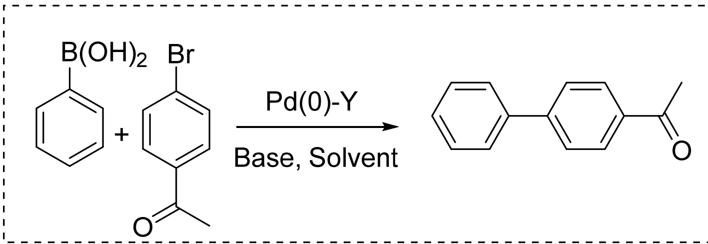
Advantages of Suzuki-Miyaura Coupling Reaction

The Suzuki coupling reactions are advantageous because of the easy availability of reactants involved, mild reaction conditions, the stability of the reagents in water, tolerance of a broad range of functional groups concerning the reaction. Also, the reaction is easy to use both in aqueous and heterogeneous conditions, with a very small amount of catalysts required to carry-out the reaction. It can also be carried out as one-pot synthesis. Further, the reaction is a non-toxic reaction and a potential candidate to be pronounced as a green reaction.[13,14]

Advantages of Heterogeneous Catalyst over Homogeneous Catalyst

The advantage of the heterogeneous catalyst over the homogeneous catalyst is in terms of separating the catalytic species from the reaction mixture. Also, in terms of recyclability of catalyst, the heterogeneous catalyst is found to be advantageous over the homogeneous catalyst. Further, heterogeneous catalyst provides large surface area for catalysis.[1-3] Some of the literature based on palladium supported on zeolites/hybrid materials are discussed below:

Corma *et al.*[15] used Pd exchange zeolites for the Suzuki coupling of bromo-derivatives with phenylboronic acid using potassium carbonate as a base. Artok *et al.*[16] designed a catalyst using $Pd(NH_3)_4^{2+}$ as ion and exchanged with NaY-zeolite. They reported that the reaction gave excellent yields with bromo-derivatives using a low load of catalyst, while a load of catalyst need to be increased 10-100 times in case of chloro-derivatives due to the strong bond dissociation energy associated with C-Cl bond. Ryoo *et al.*[17] compared the activity of microporous and mesoporous Pd-exchanged zeolites and found that the mesoporous materials exhibited enhanced conversion due to easy diffusion of bulky substituents into the cavity of mesopores as compared to micropores.



Scheme 5. Suzuki-Miyaura coupling using Pd-exchanged zeolite-Y.

Nowadays, most of the researchers have shifted their attention to bimetallic catalyst rather than their monometallic counterparts (Scheme 5). Several hybrid bimetallic structures alloyed with Pd has been designed and synthesized for such processes. The motive behind the alloying is for the enhancement in the activity, due to synergistic effect displayed by the two metals.[3-5] It is well known that this materials on support, on further hybridization with CNTs, graphene oxides, MWCNTs had demonstrated enhanced activity due to increased conductivity, surface area, etc.[18]

Conclusion

In conclusion, this chapter briefly describes the several advances in the Suzuki Miyaura Cross-coupling reaction. Several ligand systems used for SMCC reaction has also been discussed in this chapter. Furthermore, these porous materials are easily recycled, separated from the reaction mixture, environmentally viable and hence are measured as a green catalyst.

References

[1] Huang, Y. B., Wang, Q., Liang, J., Wang, X., and Cao, R., Soluble metal-nanoparticle- decorated porous coordination polymers for the homogenization of heterogeneous catalysis. *Journal of the American Chemical Society*, 138(32), 10104-10107, **2016**.

[2] Dhakshinamoorthy, A., Asiri, A. M., and Garcia, H., Metal-organic frameworks catalyzed C–C and C–heteroatom coupling reactions. *Chemical Society Reviews*, 44(7), 1922-1947, **2015**.

[3] Ai, Y., Li, X., Ji, Y., Song, W. G., and Luo, Y., Hydrophobicity and hydrophilicity balance determines shape selectivity of Suzuki coupling reactions inside Pd@ meso-SiO_2 nanoreactor. *The Journal of Physical Chemistry C*, 120(19), 10244-10251, **2016**.

[4] Morales-García, Á., Rubeš, M., and Nachtigall, P., The interaction of Pd clusters with the bulk and layered two-dimensional silicalite-1 supports. *Catalysis Today*,277(1), 108–117, **2016**.

[5] Min, B. K., Santra, A. K., and Goodman, D. W., Understanding silica-supported metal catalysts: Pd/silica as a case study. *Catalysis Today*, 85(2), 113-124, **2003**.

[6] Miyaura, N., Yanagi, T. and Suzuki, A., The palladium-catalyzed cross-coupling reaction of phenylboronic acid with haloarenes in the presence of bases. *Synthetic Communications*, 11, 7, 513-519, **1981**.

[7] Miyaura, N. and Suzuki, A., Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chemical Reviews*, 95, 7, 2457-2483, **1995**.

[8] Miyaura, N. and Suzuki, A., Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chemical Reviews*, 95, 2457-2483, **1995**.

[9] Hillhouse, J.H. and Rickleton, W.A., Cytec Technology Corp. Preparation of mono-and di-arylphosphines. U.S. Patent 6(563), 005, **2003**.

[10] Bedford, R.B. and Welch, S.L., Palladacyclic phosphinite complexes as extremely high activity catalysts in the Suzuki reaction. *Chemical Communications*, 1, 129-130, **2001**.

[11] Netherton, M.R., Dai, C., Neuschütz, K. and Fu, G.C., Room-temperature alkyl– alkyl suzuki cross-coupling of alkyl bromides that possess β hydrogens. *Journal of the American Chemical Society*, 123(41), 10099-10100, **2001**.

[12] Maluenda, I. and Navarro, O., Recent developments in the Suzuki-Miyaura reaction: 2010–2014. *Molecules*, 20(5), 7528-7557, **2015**.

[13] Suzuki, A. Organoborane coupling reactions (Suzuki coupling). *Proceedings of the Japan Academy, Series B*, 80(8), 359-371, **2004**.

[14] Paul, S., Islam, M.M. and Islam, S.M., Suzuki–Miyaura reaction by heterogeneously supported Pd in water: recent studies. *RSC Advances*, 5, 42193-42221, **2015**.

[15] Corma, A., García, H. and Leyva, A., Bifunctional palladium-basic zeolites as catalyst for Suzuki reaction. *Applied Catalysis A: General*, 236, 179-185, **2002**.

[16] Durgun, G., Aksın, Ö. and Artok, L., Pd-loaded NaY zeolite as a highly active catalyst for ligandless Suzuki–Miyaura reactions of aryl halides at low Pd loadings under aerobic conditions. *Journal of Molecular Catalysis A: Chemical*, 278, 189-199, **2007**.

[17] Choi, M., Lee, D.H., Na, K., Yu, B.W. and Ryoo, R., High Catalytic Activity of Palladium (II)-Exchanged Mesoporous Sodalite and NaA Zeolite for Bulky Aryl Coupling Reactions: Reusability under Aerobic Conditions. *Angewandte Chemie*, 121, 3727-3730, **2009**.

[18] Resasco, D.E., Ruiz, M.P. and Faria, J., Multiwall Carbon Nanotubes (MWCNT): Production, Analysis and Application. *AZONANO*, **2013**.