

Chapter - 6

Zeolite-Based Nanocomposites in Asymmetric Synthesis, C-Cl Bond Activation, and Methanol Oxidation

Mukesh Sharma, Biraj Das, Mitu Sharma and Kusum K Bania

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

Abstract—*Different types of zeolitic materials like transition-metal encapsulated, nanoparticles and nanocomposites have been discussed along with their applications. The main interest has been enclosed within some of the thrust areas like enantioselective reactions, alcohol oxidation, and C-Cl bond activation in Suzuki Miyaura Cross-Coupling reaction.*

Introduction

Aluminosilicate like zeolites are considered as an important class of irreducible oxide support that has extensively gained attention in the field of heterogeneous catalysis due to its high surface area ($\sim 400\text{m}^2/\text{g}$) and strong metal-support interaction (SMSI) than other reducible oxides like titanium dioxide (TiO_2), vanadium oxides (VO_x) etc. Another important phenomenon is the formation of silicides that has gained attention because of the importance of the metal-silica interface. Moreover, the

silicide formation has also been found to alter the selectivity and catalytic activity of many reactions. For instance, the formation of palladium silicides has been found to enhance the selectivity in the isomerization of neopentane.¹⁻⁶ In addition to this, the mesopores of silica provide a better way for the heterogenization of larger cations like Mo and W that are highly used as active metals for various oxidation processes. Recently, Samantaray *et al.* reported for a highly active W/Zr catalyst supported on silica for the metathesis of n-decanes.⁷ Manganese chiral Schiff base complexes supported in various mesoporous silica-based materials have been found to show better catalytic activity in various essential organic transformations such as in styrene epoxidation and oxidation of naphthol to BINOLs, etc.^{8,9}

Another important class of silicon-based materials is zeolites which are crystalline 3D aluminosilicates having pore diameters of around 10 Å and possesses greater surface area (~600 m²/g). Depending on the Si/Al ratio of their framework, synthetic faujasite zeolites are sub-divided into X (Si/Al= 2-3) and Y (Si/Al= greater than 3) zeolites. One of the important characteristics of zeolite is that they possess high transition state that stabilizes various active intermediates species which are formed inside their cavities resulting in the selectivity of the product. Furthermore, these porous materials are easily recycled, separated from the reaction mixture, environmentally viable and hence are considered as one of green catalyst (Figure 1).⁹

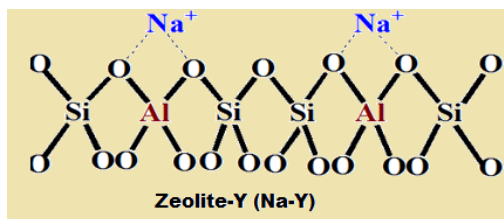


Figure 1. Structure of zeolite-NaY.

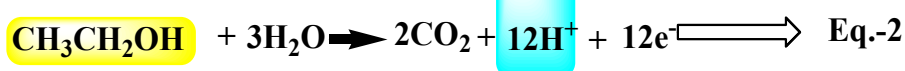
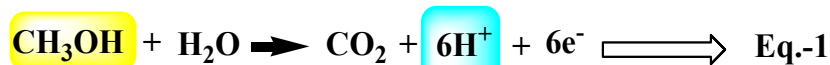
Leaching of toxic metals can also be tackled with the use of such solid materials that are nowadays a major concern in the field of homogeneous catalysis. Due to the uniformities in the structure of this type of materials, several metal complexes and clusters existing in their cages might be easier to characterize.^{3,9} R. M. Barrer synthesized the first zeolite-Y in 1948 which has been considered as the most important advances in the field of catalysis for the heterogenization of homogeneous metal complexes.¹⁰ Herron reported probably the first zeolite-Y encapsulated transition metal complexes via “*Ship in a bottle*” (SIB) method.¹¹ Several stimulating works so far have been reported on encapsulation or immobilization of transition metal complex inside the cages of zeolite-Y.^{3,9} Till now, innumerable researchers have reported for designing of various metal complexes with different ligands and metal complexes within the supercage of zeolite-Y.^{3,12,13} The main application of zeolite-Y supported metal complexes systems are considered in particular hydrogenation, partial oxidation, cross-coupling reaction, etc.^{8,9} Several metal-Schiff base complexes have also been used in asymmetric Henry reaction with high catalytic activity and enantioselectivity.^{3,12,13} Pd supported Si-based materials have also been used for Suzuki cross-coupling reaction.^{4,5} Many reports have been

described for the cross-coupling reactions supported on carbon, oxides-based material, etc., but there is a big problem of leaching of metal particles which resulted in the depletion of their catalytic activity.¹⁴ Henceforth, encapsulation of metal complexes inside the nanocavities of zeolite-Y can be a strikingly eco-friendly technique for heterogenization; since no leaching is observed when the complex is confined entirely in the nanopores of zeolite-Y.

Bimetallic nanoparticles due to the various excellent results in the early 1990s have received widespread attention for hydrogenation reactions, C-H bond activation, C-C coupling reactions, electrocatalytic oxidation of alcohols, and various environmental catalytic processes.^{1,2,7} The size, shape and composition-controlled bimetallic nanoparticles display greater catalytic performance over particles of random size, shape, and composition of their monometallic counterparts. Recently, Kaminski *et al.* reported for the complete oxidation of methanol with Au and Cu bimetallic supported on modified zeolite MCM 22.¹⁵

Another important thrust area in the field of catalysis is the generation of hydrogen fuel as a renewable source of energy. Pt-catalyst-based proton-exchange membrane fuel cell (PEMFCs) denotes one of the most broadly used and well-explored fuel-cell systems. Catalytic oxidation of alcohol via oxygen can be used to produce electricity in various electrochemical devices that are generally recognized as direct alcohol fuel cells (DAFCs). Considerably, the use of methanol as the fuel (direct methanol fuel cells (DMFCs)) for PEMFCs has engrossed massive attention

due to its comparatively high energy density as compared to gasoline and ease of transportation. Apart from methanol, ethanol is the second most extensively studied alcohol that is known as a direct ethanol fuel cell (DEFC). The products of alcohol fuel cells should be CO₂ and H₂O to release the maximum possible energy.^{16,17} Under usual conditions, oxidation of 1 mol of methanol should generate 6 mol of electrons and 1 mol of CO₂ with a standard reversible potential E⁰ of 0.016 V vs SHE, as in equation 1, while for ethanol, 2 mol of CO₂ and 12 mol of electrons are generated with an E⁰ value of 0.084 V vs SHE, according to equation 2.



Unluckily, the electro-oxidation of methanol and ethanol are kinetically slow processes with overpotentials of 0.3–0.4 V for ethanol and 0.45 V for methanol despite using all advanced catalysts. Usually, platinum (Pt) is employed as the catalyst in acidic media in DMFC or DEFC devices. However, Pt on its own is not a highly efficient catalyst due to the poisoning effect from the deeply adsorbed species such as CH(ad), CH₃(ad), and CO(ad) generated during oxidation.¹⁸

Due to the crystalline nature composed of Si and AlO₄⁻ tetrahedral, constant electronegativity, multidimensional microporosity, bimetallic exchanged zeolites are one of the most accomplished catalysts in DAFC's. The various advantages of using zeolites over carbon materials are:

- it provides electrodes with lower ohmic power loss because of its high surface area and channel structure.
- it also reduces the cost of the catalyst and acts as a green catalyst.
- it also prevents the catalyst particle from agglomeration.
- more hydrophilic than carbon.
- higher water retention ability.

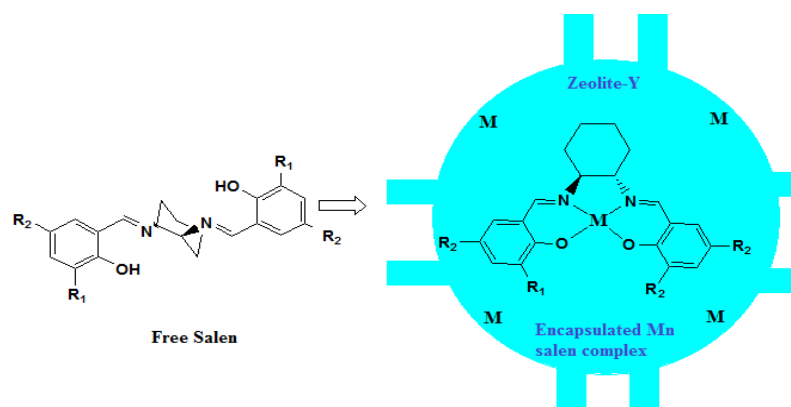
Different Applications of Metal-based Aluminosilicates

Enantioselective Synthesis. The importance of these fields can be made since the Nobel Prize in Chemistry for the year 2001 has been awarded one half to Karl Barry Sharpless, and the other half has been equally shared by Ryoji Noyori and William S. Knowles for their tremendous work in the field of asymmetric synthesis. Asymmetric synthesis has gained tremendous consideration due to its hasty growth of the pharmaceutical industries in the last two decades.^{2,3,8,9,12} Homogeneous asymmetric catalyst despite having importance in asymmetric catalysis has several disadvantages like catalyst separation and recyclability which often makes difficulty for various industrial processes since the chiral catalyst are quite expensive. So, recent focused has been made in the heterogenization of costly chiral homogeneous catalysts that supplies an opportunity for easy separation and easy purification of the product.

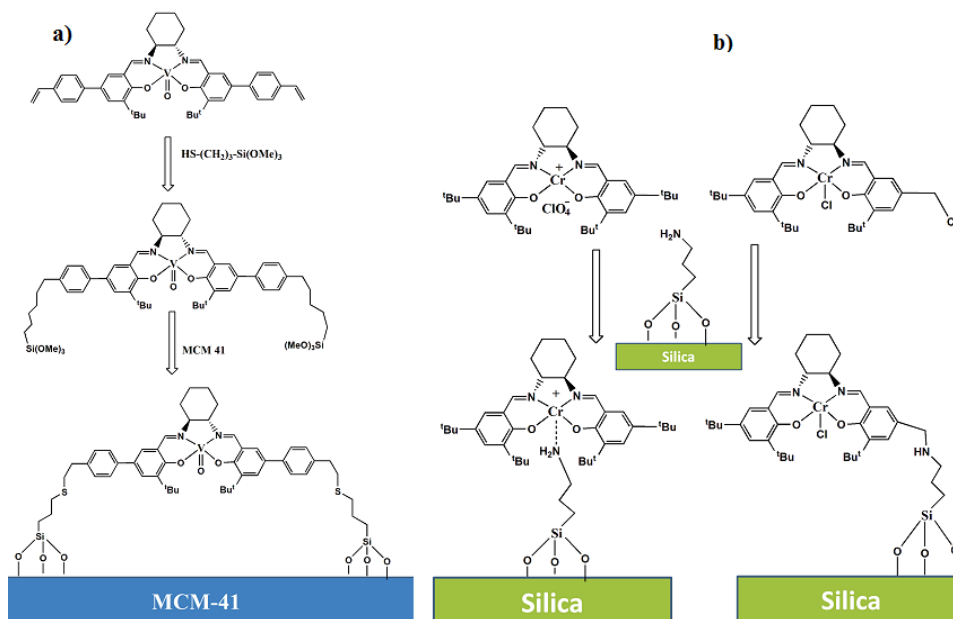
Furthermore, for heterogenization of homogeneous catalysts, several techniques via accumulating the chiral catalysts in the pores or cavities of the porous mantles like silica, zeolites, MCM-41 are now grabbing tremendous attention in the field of heterogeneous catalysis. Due to the

porous supports, such as microporous materials (zeolites) and mesoporous materials (silica) offers a large surface area, uniformity in the pore size distribution. Silica and zeolites are one of the most important porous materials support for immobilizing and encapsulation of the homogeneous catalysts. Because of the confinement effect, one can easily improve the enantioselectivity during the reaction.^{3,7-9}

Jacobsen's findings in the early 1990s with manganese(III)Salen-like ligands as catalysts for the enantioselective epoxidation of isolated alkenes was a boost for the enantioselective reaction. His contributions with Katsuki's thereafter allowed various transition metal Schiff based complexes to be used as chiral-directing catalysts that are useful for the development of enantiopure drugs and various biologically active molecules. After that, various supported manganese-based catalysts were reported.¹⁹ Sabatier *et al.* reported the encapsulation of chiral manganese Schiff complexes inside the zeolite-Y as shown in Scheme 1.²⁰ The Mn-Salen complex formed in the zeolite supercage shows no leaching of active site during the epoxidation reaction. Baleizao *et al.* similarly synthesized styrene derivative V(Salen) complexes supported on MCM 41,²¹ Scheme 2a.



Scheme 1. Zeolite-Y encapsulation of chiral metal-Salen complex *via* flexible ligand method.



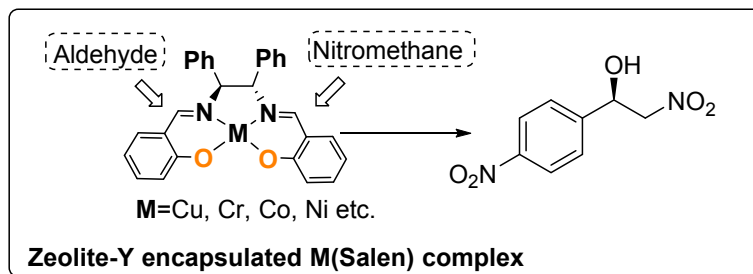
Scheme 2. a) Styrene derivative of V(Salen) complex supported on MCM-41, and b) chiral Cr(Salen) complex supported on silica.

Similarly, their groups also reported a chiral Cr (Salen) complexes supported on silica (SiO_2) which acts as catalysts for ring-opening reactions,

Scheme 2b.²¹ However, their enantiomeric excess (ee) was found to be very poor. Among various important asymmetric reactions, Henry reaction or nitro-aldol reaction is considered as a significant class of organic transformations due to the wide application of the aldol product in various natural product syntheses.^{2,3,12} Diverse range of homogeneous and heterogeneous chiral catalysts has been executed to attain such transformations,¹³ but still, a sparse report are found to exhibit good catalytic activity along with the recyclability. However, limited success had been achieved in research to develop highly flexible, chiral, heterogeneous catalysts for asymmetric organic transformations. Immobilized chiral catalysts or chiral modifiers can detach from much other solid support, resulting in weak or no surface chirality. So, the development of original and alternative methods to generate surfaces with chiral activity is still a great challenge. Different approaches have been investigated to influence the synthesis of chiral products. Recently, Deka and his group synthesized various transition metal chiral Schiff base complexes inside zeolite-Y for Henry reactions with high catalytic activity and enantiomeric excess (ee), Scheme 3. Zeolite-Y-encapsulated chiral Schiff-base complexes of copper were found to show better catalytic activity.^{3,12,13}

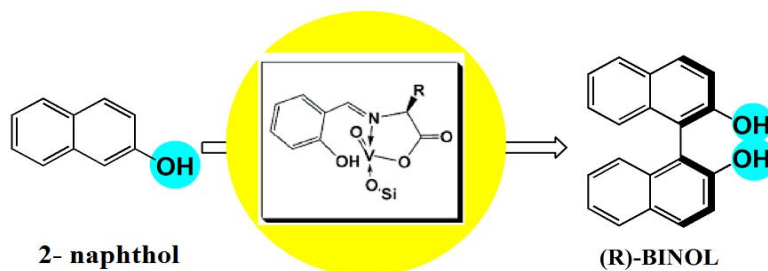
Similarly, asymmetric oxidative coupling of 2-naphthol is one of the most atom cost-effective straightforward pathways to obtain to BINOL. The importance of BINOLs lies in the fact that these acts as extremely effective chiral auxiliaries or chiral pools for the synthesis of other chiral potent drugs.^{9,22} Consequently, a large amount of homogeneous and

heterogeneous catalysts has been so far developed which in most cases, either leads to achiral products or with some byproducts. Therefore, designing newer catalysts for such oxidative coupling reaction is an ongoing process.



Scheme 3. Asymmetric Henry reaction inside zeolite-Y with chiral M(Salen) complex.

Tada *et al.* recently developed a chiral self dimerized complex of vanadium supported on SiO_2 .²³ Similarly, recent studies have shown that the chiral vanadium (Salen) complex can act as a better catalyst for aerobic oxidative coupling of 2-naphthol, Scheme 4.



Scheme 4. Vanadium catalyst supported on SiO_2 for oxidative coupling of 2-naphthol.

C-Cl Activation. Heck, Negishi and Suzuki have marked immense influence on palladium (Pd) catalyzed carbon-carbon bond formation reactions

which are of great importance and have been used expansively in the synthesis of various pharmaceuticals, natural products, high tech materials, etc.^{2,14} Suzuki-Miyaura cross-coupling reaction is considered to be the most efficient available methods among all which involves the formation of a new carbon-carbon bond. Mild conditions related to these reactions and great tolerance of a wide variety of functional groups mostly lead to their extensive use. Apart from these advantages, this route allows easy removal of boron-containing byproducts in comparison to other highly used organometallic reagents. Over the last few decades, Pd is known to be the most proficient metals for the C-C bond formation reactions.^{2,4,14} But recently, almost all researchers have shifted their attention to supported Pd nanoparticles over Pd complexes because of their enhanced catalytic activity due to its high surface to volume ratio. In this regard, zeolites have a large surface area and uniform micropores that can accommodate dispersed metal clusters, leading to a high surface-to-volume ratio. The plausible mechanism for C-Cl activation is shown in Figure 2.

Aryl bromides, iodides have been extensively explored as a substrate for this reaction since they are easy to activate via active Pd(0) species. However, the activation of aryl chlorides is still a challenging task. Aryl chlorides are of great interest, and their widespread use in biphenyl is mainly due to its easy availability and less cost than other aryl halides.¹⁴ The C-C bond activation is facilitated by using various costly ligands such as N-Heterocyclic carbenes, electron-rich phosphanes, etc. which are not

recyclable and results in contaminated products that are mostly discarded by pharmaceuticals industry. Pd nanoparticles supported on various silicon and carbon-based materials such as zeolites, carbon nanotubes, graphenes, and its oxides allows one to prepare ligand-free heterogeneous catalyst that has attracted the attention of many researchers because they possess the advantage of reusability and can replace costly homogeneous counterparts. Kumbhar *et al.* reported a Pd modified zeolite for C-Br activation with good catalytic activity and recyclability. They were able to activate C-Cl bond having yield less than 40%.²⁴ Similarly, Okumura *et al.* recently reported for such coupling reactions with aryl bromides with ultra-stable zeolite-Y loaded on Pd, Scheme 5b. They stated that Pd gets stabilized by Al sites of the Y-type zeolite. They also reported that Pd species instantly change to PdO clusters on exposed to air under thermal conditions,²⁵ (Scheme 5a).

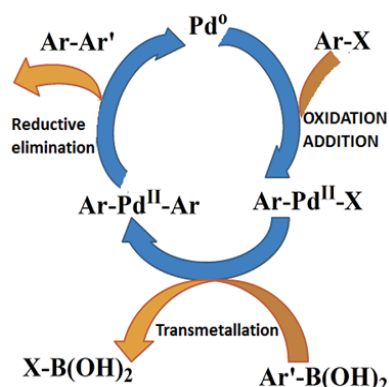
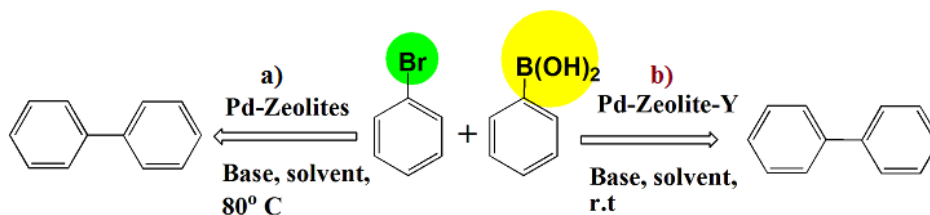


Figure 2. A plausible mechanism for Suzuki Miyaura cross-coupling reaction.

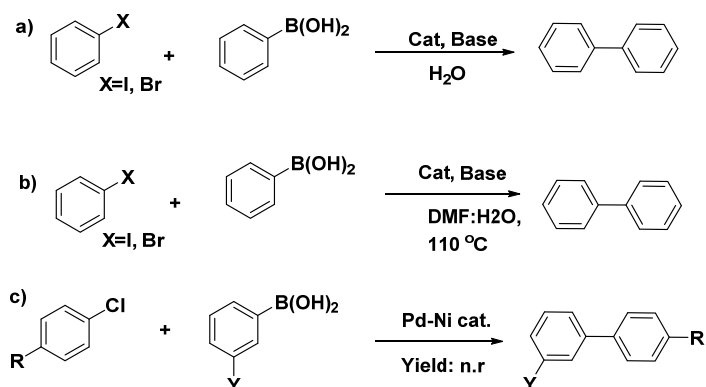


Scheme 5. Suzuki reactions via a) Pd supported zeolites and b) Pd ultra-stable zeolite-Y.

Mahdavi *et al.* recently reported polyacrylamide-g-reduced graphene oxide supported Pd nanoparticles as a highly efficient catalyst for Suzuki–Miyaura reactions in water, Scheme 6a. However, they mostly focused on C-Br and C-I activation and the procedure for catalyst preparation were also extensively lengthy.²⁶ Similarly, Rathi *et al.* synthesized ultra-stable Pd nanoparticles supported on iron oxide resulting in good yield with C-Br and C-I derivatives, but the yield for C-Cl activation was as usual quite poor in spite of providing quite high temperature²⁷ (Scheme 6b). Dhankar *et al.* have also reported a highly efficient Pd-Ni catalyst showing almost negligible yield for C-Cl activation²⁸ (Scheme 6c).

All these reports display that activating C-Cl bond is still not an easy task for most of the researchers. The activation of inexpensive aryl chlorides *via* a heterogeneous ligand-free, TBAB free Pd catalyzed C-C cross-coupling reactions in water leads to the recyclability of the catalyst along with the formation of less contaminated byproducts. Pd nanoparticles supported on carbon-based materials are of great interest but has been discarded due to various reports of Pd leaching into solutions. Recently, Duan *et al.* reported the stabilization of palladium

nanoparticles by adding inert silica into mesoporous carbon matrix.¹⁴ Activation of aryl chlorides are known to be facilitated by Pd nanoparticles that are in the range of 3-5 nm. Further catalytic enhancement has been achieved by providing transition metal oxide nanoparticles in carbon matrix which shows good conversion of biphenyls. Similarly, Huang *et al.* reported for ultra-stable Pd nanoparticles for facile C-Cl activation.¹



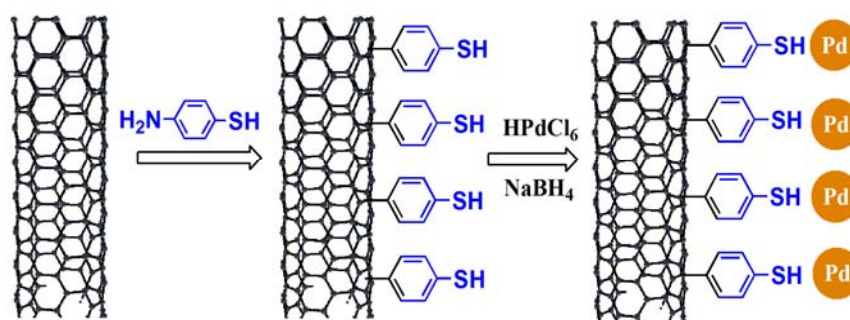
Scheme 6. Suzuki reaction with a) graphene oxide supported nanoparticles, b) ultra-stable Pd nanoparticles supported on iron oxide, and c) Pd-Ni alloy nanoparticles.

So, the activation of aryl chlorides in aqueous, ligand-free, TBAB free conditions *via* palladium nanoparticles supported on metal oxide nanoparticles over the zeolite matrix are one of the fascinating topics in the field of C-Cl activation. Therefore, knowing the nature of the mechanism and having a deep understanding of where the active sites are and how the actual reaction at those sites are taking place is still one of the most important factors for the designing of new efficient catalysts for the Suzuki-Miyaura cross-coupling reactions.

Electrocatalytic oxidation of methanol. Due to the undeniable advantages over comparable devices fed with hydrogen, direct alcohol fuel cells (DAFCs) are drawing cumulative importance as power sources for portable applications. Various alcohols such as methanol, ethanol, ethylene glycol, and glycerol are gathering vast attention due to their much facile storage and transportability, cost-effectiveness as compared to hydrogen,^{15,16} Figure 3. Most importantly, it is the high volumetric energy density exhibiting ability which makes them superior in comparison to hydrogen. On the other hand, the oxidation kinetics of any alcohol is much slower and still H₂-fueled polymer electrolyte fuel cells (PEMFCs) exhibit superior electrical performance as compared to DAFCs with comparable electroactive surface areas. Various results based on Pt till now has been reported which despite showing excellent results holds several disadvantages like cost ineffectiveness, formation of several inactive intermediates and in recyclability that forced the researchers to adopt a new alternate second approach of having less-expensive metals, such as Pd in replacement for Pt.^{6, 17}

Yin *et al.* also suggested developing designer nanostructures of the catalyst by using very specific supports. They developed a bimetallic Pd-Cu nanocatalyst that shows tremendous enhancement in electro-catalytic activity for methanol oxidation.⁹ Similarly, better electrochemical activities were shown by bimetallic catalyst over the respective monometallic counterparts has also been well conveyed for the Pt-Ru system.³⁰ Li *et al.*

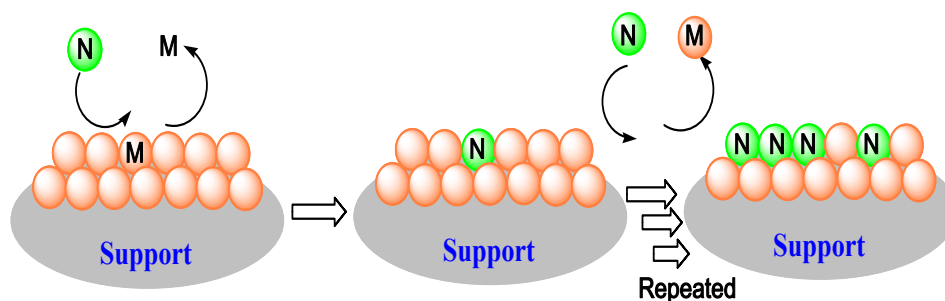
developed self-assembly of Pd nanoparticles on MWCNTs functionalized with mercaptobenzene moieties, Scheme 7. Other inorganic supports like nanotube morphology have also been effectively employed to prepare Pd-based electrocatalysts for DAFCs. Li *et al.* have described the synthesis of Pd particles supported on a large variety of nanotubes, including MWCNTs, TiO₂ nanotubes, vanadium oxide nanotubes,³¹ etc. Recently, Suntivich *et al.* also reported for tuning of Au–Pt bimetallic nanoparticles for enhanced methanol electro-oxidation.³²



Scheme 7. Self-assembly synthesis of Pd nanoparticles on functionalized MWCNTs.

Various excellent results on bimetallic Pd nanoparticles for hydrogenation reactions, C-H bond activation, oxidative addition, C-C coupling reactions, and environmental catalytic processes have gained massive attention since the 1990s.^{11,19,30} The size, shape and composition-controlled bimetallic nanoparticles displayed greater catalytic performance over particles of random size, shape, and composition. In fuel cell applications, bimetallic alloys of Pd with early transition non-noble metals, such as Pd–Ni, have not only exhibited higher catalytic activities compared

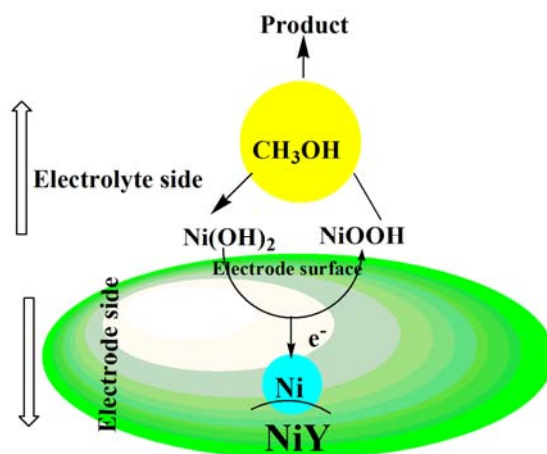
with monometallic Pd catalysts but can be cost-effective and less harmful. The spontaneous deposition (SD) of noble metals onto less noble metal surfaces is one of the most emerging techniques for constructing new catalyst. This technique is sometimes referred to as surface replacement reaction (SRR), Scheme 8.³³ Recently, Miao *et al.* reported for the synthesis of novel Pd-Ni catalyst supported on silica showing remarkable electrocatalytic activity in alkaline media.³⁴ Ojani *et al.* reported a Ni(II) exchanged zeolite-Y for the electrochemical oxidation of methanol,³⁵ (Scheme 9). Whiting *et al.* recently reported for the oxidation to methyl format via Au-Pd supported on TiO₂.³⁶



Scheme 8. Schematic metal deposition onto metal particles via redox transmetalation.

Similarly, various reports have been found where this bimetallic couple shows enhanced activity which not only reduces the cost but could also provide faster kinetics in various alcohol oxidation processes. So, designing via dilution of Pd with non-noble metals is a smart catalytic design capable of rapidly oxidizing alcohols on anode electrodes. Therefore, designing of a proficient bimetallic electrocatalyst which could lessen the amount of

adsorbed intermediates and thereby advances the electrocatalytic oxidation of alcohol is still an interesting topic in DAFs.



Scheme 9. Schematic representation of the electrocatalytic oxidation of methanol on the surface of Ni-NiY/Carbon paste electrode (CPE).

Conclusion

A brief survey on various zeolite-based nanocomposites along with their applications in different organic transformations like Henry reaction, C-Cl bond activation and designing of DAFs is discussed. The role of zeolite-Y in the aforementioned catalytic processes has also been highlighted in each section.

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. Sharma, M., Das, B., Karunakar, G. V., Satyanarayana, L., and Bania, K. K. Chiral-Ni-Schiff base complexes inside zeolite-Y and their application in asymmetric Henry reaction: Effect of initial activation with microwave irradiation. *The Journal of Physical Chemistry C*, 120(25), 13563–13573, **2016**.
4. 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-SiO₂ nanoreactor. *The Journal of Physical Chemistry C*, 120(19), 10244-10251, **2016**.
5. 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**.
6. 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**.
7. Samantaray, M. K., Dey, R., Kavitha, S., Abou-Hamad, E., Bendjeriou-Sedjerari, A., Hamieh, A., and Basset, J. M. Synergy between two metal catalysts: A highly active silica supported bimetallic W/Zr catalyst for metathesis of n-decane. *Journal of the American Chemical Society*, 138, 8595–8602, **2016**.
8. Mandal, M., Nagaraju, V., Sarma, B., Karunakar, G. V., and Bania, K. K., Enantioselective epoxidation of styrene by manganese chiral schiff base complexes immobilized on MCM-41. *ChemPlusChem*, 80(4), 749-761, **2015**.
9. Mandal, M., Nagaraju, V., Karunakar, G. V., Sarma, B., Borah, B. J., and Bania, K. K., Electronic, conjugation, and confinement effects on structure, redox, and catalytic behavior of oxido-vanadium (IV) and-(V) chiral Schiff base complexes. *The Journal of Physical Chemistry C*, 119(52), 28854-28870, **2015**.
10. Barrer, R. M. Synthesis of Molecular Sieve Zeolites. *Molecular Sieves, London, England, Soc. Chem. Ind., London*, 39-46, **1968**.
11. Herron, N. and Tolman, C. A. A highly selective zeolite catalyst for hydrocarbon oxidation. A completely inorganic mimic of the alkane. Omega hydroxylases. *Journal of the American Chemical Society*, 109(9), 2837-2839, **1987**.
12. Bania, K. K., Karunakar, G. V., Goutham, K., and Deka, R. C. Enantioselective Henry reaction catalyzed by “ship in a bottle” complexes. *Inorganic Chemistry*, 52(14), 8017-8029, **2013**.
13. Deka, J., Satyanarayana, L., Karunakar, G. V., Bhattacharyya, P. K., and Bania, K. K. Chiral modification of copper exchanged zeolite-Y with cinchonidine and its

- application in the asymmetric Henry reaction. *Dalton Transactions*, 44(48), 20949-20963, **2015**.
14. Duan, L., Fu, R., Xiao, Z., Zhao, Q., Wang, J. Q., Chen, S., and Wan, Y. Activation of aryl chlorides in water under phase-transfer agent-free and ligand-free Suzuki coupling by heterogeneous palladium supported on hybrid mesoporous carbon. *ACS Catalysis*, 5(2), 575-586, **2015**.
 15. Kaminski, P., Sobczak, I., Decyk, P., Ziolek, M., Roth, W. J., Campo, B., and Daturi, M. Zeolite MCM-22 modified with Au and Cu for catalytic total oxidation of methanol and carbon monoxide. *The Journal of Physical Chemistry C*, 117(5), 2147-2159, **2013**.
 16. Kamiya, K., Kamai, R., Hashimoto, K., and Nakanishi, S. Platinum-modified covalent triazine frameworks hybridized with carbon nanoparticles as methanol-tolerant oxygen reduction electrocatalysts. *Nature Communications*, 5, **2014**.
 17. Huang, W., Wang, H., Zhou, J., Wang, J., Duchesne, P. N., Muir, D., Zhang, P., Han, N., Zhao, F., Zeng, M., and Zhong, J. Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum-nickel hydroxide-graphene. *Nature Communications*, 6, **2015**.
 18. Liu, Y., Zhao, S. F., Guo, S. X., Bond, A. M., Zhang, J., Zhu, G., Hill, C. L., and Geletii, Y. V. Electro oxidation of ethanol and methanol using the molecular catalyst $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]_{10}$. *Journal of the American Chemical Society*, 138(8):2617-2628, **2016**.
 19. Zhang, W., Loebach, J. L., Wilson, S. R., and Jacobsen, E. N. Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes. *Journal of the American Chemical Society*, 112(7), 2801-2803, **1990**.
 20. Sabater, M. J., Corma, A., Domenech, A., Fornés, V., and García, H. Chiral salen manganese complex encapsulated within zeolite Y: A heterogeneous enantioselective catalyst for the epoxidation of alkenes. *Chemical Communications*, 14, 1285-1286, **1997**.
 21. Baleizao, C. and Garcia, H. Chiral salen complexes: an overview to recoverable and reusable homogeneous and heterogeneous catalysts. *Chemical Reviews*, 106(9), 3987-4043, **2006**.
 22. Narute, S., Parnes, R., Toste, F. D., and Pappo, D. Enantioselective oxidative homo- and cross-coupling of 2-naphthols catalyzed by chiral iron phosphate complexes. *Journal of the American Chemical Society*, 138(50), 16553-16560, **2016**.
 23. Tada, M., Kojima, N., Izumi, Y., Taniike, T., and Iwasawa, Y. Chiral self-dimerization of vanadium complexes on a SiO₂ surface for asymmetric catalytic coupling of 2-naphthol: Structure, performance, and mechanism. *The Journal of Physical Chemistry B*, 109(20), 9905-9916, **2005**.

24. Kumbhar, A., Kamble, S., Mane, A., Jha, R., and Salunkhe, R. Modified zeolite immobilized palladium for ligand-free Suzuki–Miyaura cross-coupling reaction. *Journal of Organometallic Chemistry*, 738, 29-34, **2013**.
25. Okumura, K., Mushiake, T., Matsui, Y., and Ishii, A. Suzuki coupling reactions catalyzed by PdO dispersed on dealuminated Y zeolite in air under ambient conditions. *ChemPhysChem*, 16(8):719-1726, **2015**.
26. Mahdavi, H. and Rahmani, O. Polyacrylamide-g-reduced graphene oxide supported Pd nanoparticles as a highly efficient catalyst for Suzuki–Miyaura reactions in water. *Catalysis Letters*, 146(11):2292-2305, **2016**.
27. Rathi, A. K., Gawande, M. B., Pechousek, J., Tucek, J., Aparicio, C., Petr, M., Tomanec, O., Krikavova, R., Travnicek, Z., Varma, R.S., and Zboril, R. Maghemite decorated with ultra-small palladium nanoparticles (γ -Fe₂O₃-Pd): applications in the Heck–Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes. *Green Chemistry*, 18(8), 2363-2373, **2016**.
28. Dhankhar, A., Rai, R. K., Tyagi, D., Yao, X., and Singh, S. K. Synergistic catalysis with MIL-101: Stabilized highly active bimetallic NiPd and CuPd alloy nanoparticle catalysts for C–C coupling reactions. *Chemistry Select*, 1(12), 3223-3227, **2016**.
29. Yin, Z., Zhou, W., Gao, Y., Ma, D., Kiely, C. J., and Bao, X. Supported Pd–Cu bimetallic nanoparticles that have high activity for the electrochemical oxidation of methanol. *Chemistry—A European Journal*, 18(16), 4887-4893, **2012**.
30. Radmilovic, V., Gasteiger, H. A., and Ross, P. N. Structure and chemical composition of a supported Pt–Ru electrocatalyst for methanol oxidation. *Journal of Catalysis*, 154(1), 98-106, **1995**.
31. Zhu, Z. Z., Wang, Z., and Li, H. L. Self-assembly of palladium nanoparticles on functional multi-walled carbon nanotubes for formaldehyde oxidation. *Journal of Power Sources*, 186(2), 339-343, **2009**.
32. Suntivich, J., Xu, Z., Carlton, C. E., Kim, J., Han, B., Lee, S. W., Bonnet, N., Marzari, N., Allard, L. F., Gasteiger, H. A., and Hamad-Schifferli, K. Surface composition tuning of Au–Pt bimetallic nanoparticles for enhanced carbon monoxide and methanol electro-oxidation. *Journal of the American Chemical Society*, 135(21), 7985-7991, **2013**.
33. Ge, J., Xing, W., Xue, X., Liu, C., Lu, T., and Liao, J. Controllable synthesis of Pd nanocatalysts for direct formic acid fuel cell (DFAFC) application: From Pd hollow nanospheres to Pd nanoparticles. *The Journal of Physical Chemistry C*, 111(46), 17305-17310, **2007**.

34. Miao, F., Tao, B., Sun, L., Liu, T., You, J., Wang, L., and Chu, P. K. Preparation and characterization of novel nickel–palladium electrodes supported by silicon microchannel plates for direct methanol fuel cells. *Journal of Power Sources*, 195(1), 146-150, **2010**.
35. Ojani, R., Raoof, J. B., Fathi, S. and Alami-Valikchali, S. Electrochemical behavior of Ni (II) incorporated in zeolite Y-modified carbon electrode: Application for electrocatalytic oxidation of methanol in alkaline solution. *Journal of Solid State Electrochemistry*, 15(9), 1935-1941, **2011**.
36. Whiting, G. T., Kondrat, S. A., Hammond, C., Dimitratos, N., He, Q., Morgan, D. J., Dummer, N. F., Bartley, J. K., Kiely, C. J., Taylor, S. H., and Hutchings, G. J., Methyl formate formation from methanol oxidation using supported gold–palladium nanoparticles. *ACS Catalysis*, 5(2), 637-644, **2014**.