

A Review on Polyaniline-Supported Catalyst for Organic Transformations

Satyaranjan Behera*

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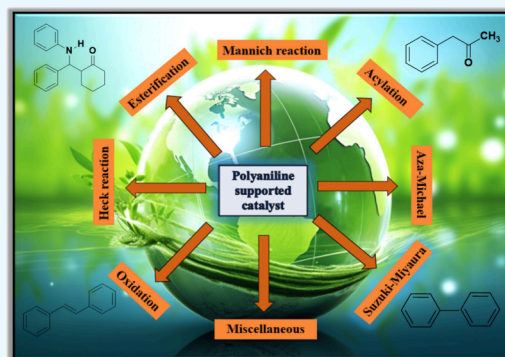
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ABSTRACT: Organic transformations are very important in synthetic organic chemistry and are used immensely in pharmaceuticals. Polyaniline is a marvelous and exceptional conducting polymer because of its extensive and valuable applications. Various modified polyaniline derivatives were developed by researchers and explored as solid heterogeneous catalysts for synthesizing important organic compounds through different organic transformations. Polyaniline-supported catalysts have many advantages: easy synthesis, environmental stability, environmental friendliness, high yield, short reaction times, the requirement for green solvent or solventless medium, and excellent reusability. In past years, polyaniline-supported catalysts have been widely used in various important organic syntheses under solvent-free or green reaction conditions. Hence, here is a comprehensive, detailed review of the application of polyaniline catalysts in organic transformations with all of their advantages and future scope.



1. INTRODUCTION

In the natural world, the synthesis of organic compounds plays a vital role and is an incredible contribution to improving human life.^{1,2} Organic molecules have irreplaceable applications in many sectors, such as natural products, drugs, and pharmaceuticals.^{3–5} In the beginning, organic compounds are achieved by various methods, which have many drawbacks, such as high cost, difficult synthesis of catalysts, using toxic catalysts or harmful solvents, and causing harm to society and the environment. The environment demands eco-friendly catalysts and green reactions in the present scenario. In the last two decades, researchers have constantly focused on achieving organic compounds using green methodology, and they have succeeded.^{6–8} Still, there is also a need to improve many green catalysts and green procedure methods for many organic transformations. In the last few decades, polymer-supported catalysts have attracted significant attention due to their efficiency, heterogeneity, low cost, easy synthesis, and reusability for the development of green methodologies.^{9–12} Out of many known polymers, polyaniline is distinguished because of its chemical and physical properties, such as good electrical properties, environmental stability, and accessible synthesis, and it has numerous applications in display devices, plastic batteries, sensors, optoelectronic devices, photonic devices, anticorrosion materials, optical storage lithography, and organic transformations.^{13–17} Due to the advantages of polyaniline, researchers have been studying it for the last few decades and have gained remarkable activity in the synthesis of organic compounds.

In this Review, we documented organic transformations catalyzed by polyaniline catalysts and showed the advantages of polyaniline and polyaniline catalysts in the last few decades.

1.1. Polyaniline. In the 19th century, scientists (F. Ferdinand Runge, Carl Fritzsche, John Lightfoot, and Henry Letheby) reported the discovery of polyaniline using chemical and electrochemical oxidation methods. John Lightfoot explicitly investigated the oxidation of aniline and the first successful commercial synthesis pathway of a dye known as “aniline black”.¹⁸ In 1862, scientist Dr. Henry Letheby discovered a “blue substance” during the electrolysis of aniline sulfate (AS), which previously was known as “aniline black”. That blue substance became colorless when treated with reducing agents and appeared green by oxidation.¹⁹ This same discovered material was later known as polyaniline (PANI). Conducting polymers have highly attracted the attention of all researchers to date. Polyaniline (PANI) is the most popular among all conducting polymer families and has distinguishable properties because of the conducting nature of the polymer. The conductivity of polyaniline makes it a valuable material for a variety of applications, including chemical sensors,^{20–23} photo-

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voltic cells,^{24,25} rechargeable batteries,^{26,27} shielding against electromagnetic interference (EMI),^{28–30} enzyme immobilization matrices,^{31,32} corrosion devices, microwave absorption,^{33–35} and gas separation membranes.^{36–38} Moreover, conducting polymers can be employed as conducting fillers in insulating polymer matrices to create composite materials that are electrically conducting. Potential applications for these composites include electrodes, electronic packaging, display devices, and barriers against electromagnetic interference (EMI).^{39–44} Moreover, polyaniline exhibits good environmental stability, ease of synthesis, a low-cost monomer, and low toxicity.⁴⁵

Polyaniline is synthesized by the oxidative polymerization of aniline by either chemical or electrochemical oxidation. Generally, the oxidation is carried out in an acidic aqueous medium having a pH below 3–4.^{46–49} Polyaniline can occur in numerous well-defined oxidation states. These states and the corresponding names of the polymers were initially proposed by Green (1864–1941) and Woodhead in 1910. Based on oxidation states, polyaniline is categorized into three types as follows.

1.1.1. Leucoemeraldine Base. A leucoemeraldine base is a form of polyaniline that is fully reduced, colorless, and an insulator. The polymer chains are comprised completely of reduced units, as shown in Figure 1.

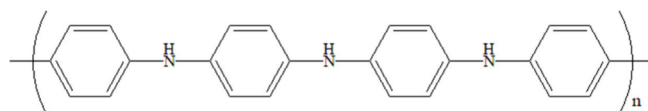


Figure 1. Leucoemeraldine base.

1.1.2. Pernigraniline Base. A pernigraniline base is a form of polyaniline that is fully oxidized, is an insulator, and is purple in color. The polymer chains are comprised completely of oxidized units, as shown in Figure 2.

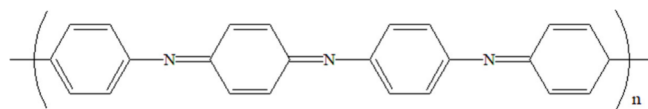


Figure 2. Pernigraniline base.

1.1.3. Emeraldine Base. Emeraldine base is the intermediate oxidation state of polyaniline, which is a good conductor and blue in color. The polymer chains are composed of an equivalent amount of alternating reduced base and oxidized base units, as shown in Figure 3.

1.2. Modification of Polyaniline. Currently, the modification of polyaniline has received significant attention from many researchers because modification leads to higher conductivity of polyaniline and surprising properties.^{50–55} The doping of polyaniline mainly increases the electrical conductivity and other properties, such as electronic, optical, and magnetic

properties.^{56,57} Out of three different types of polyanilines, the doping of polyaniline can only be possible using an emeraldine base.⁵⁸ Traditionally, many inorganic acids are used as dopants in polyaniline to make it a polyaniline salt, significantly increasing the conductivity. In recent years, several attempts have been made to improve the processability of polyaniline.

1.3. Physical and Chemical Properties of Polyaniline.

1.3.1. Physical Properties of Polyaniline. Based on the chemical structure, polyaniline exists in three forms, each exhibiting unique physical characteristics. If the polymer type is pernigraniline, polyaniline produces a blue to violet color; if the polymer form is emeraldine, it gives a blue color if it is basic and a green color if it is in its salt form. Polyaniline appears white/clear or colorless if the polymer form is leucoemeraldine. Only the emeraldine form of polyaniline exhibits strong electrical conductivity; the other forms do not exhibit any discernible conductivity.⁵⁹ The electrical conductivity of polyaniline modified by different materials is described in Table 1.

Table 1. Electrical Conductivity Properties of Modified Polyaniline

sl. no.	catalyst	dopant	conductivity (S/cm)	ref
1	PANI-Au	gold	2.13×10^{-4}	61
2	GO-PANI	graphene oxide	0.1	62
3	PANI-TiO ₂	titanium dioxide	1×10^{-5}	63
4	PANI/MWCNTs	multiwall carbon nanotubes (MWCNTs)	2.28	64
5	PANI-NC	nanoclay (NC)	2.143	65
6	PVA/PANI/Ni	polyvinyl alcohol/nickel NPs	4.9	66
7	PANI-NA	nicotinic acid	0.63	67
8	PANI-Au-CSA	camphor sulfonic acid	5.42×10^{-3}	61
9	PANI-EB	undoped	13.8×10^{-5}	68
10	PANI-H ₂ SO ₄	sulfuric acid	2.0×10^{-2}	75
11	PANI-HBF ₄	fluoroboric acid	1.0×10^{-2}	75
12	PANI-HClO ₄	perchloric acid	5.0×10^{-3}	75
13	PANI-HCl	hydrochloric acid	5.0×10^{-4}	75
14	PANI-PTSA	<i>p</i> -toluenesulfonic acid	1.0×10^{-2}	75
15	PANI-SSA	sulfosalicylic acid	1.0×10^{-2}	75
16	PANI-FeCl ₃	ferric chloride	2.4×10^{-3}	75
17	PANI-ZnI ₂	zinc iodide	3.8×10^{-6}	75

Regarding solubility, dimethylformamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone are soluble in PANI, while water, acetone, ethanol, and other solvents do not dissolve any form of polyaniline.^{59,60}

1.3.2. Chemical Properties of Polyaniline. The chemical stability of the polyaniline is good when polyaniline is doped with either acids or bases, with changes in the electrical and electrochemical properties of the polyaniline.⁶⁹ The polymer main chain is not involved in the chemical reaction during the processes of doping and dedoping. For that reason, polyaniline shows good chemical resistance toward acidic and basic

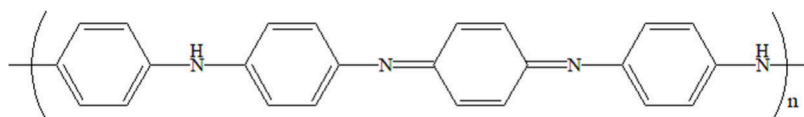


Figure 3. Emeraldine base.

solutions, where it does not go through any type of chemical reaction or chemical degradation.

1.4. Synthesis of Polyaniline. There are two main types of oxidation methods used to synthesize polyaniline. These are polymerization and either chemical or electrochemical oxidation. The details of the techniques are discussed below.

1.4.1. Chemical Oxidative Polymerization of Aniline. Polyaniline can be chemically synthesized by oxidative aniline polymerization in an acidic medium using oxidizing agents. Oxidative polymerization is the most commonly used method because it is facile, less time-consuming, and economical. Various oxidants have been used for oxidative polymerization, such as ammonium peroxydisulfate,⁷⁰ hydrogen peroxide, ferric chloride,⁷¹ ceric nitrate, and sulfate.⁷² This method is simple in that the synthesis is based on the simultaneous mixing of an aqueous aniline solution prepared in acidic media and an ammonium peroxy disulfate solution at ambient temperature, followed by filtration of polyaniline precipitates and drying.

1.4.2. Electrochemical Polymerization of Aniline. In this era of advanced technology, electrochemical polymerization has attracted attention due to its many advantages, such as providing control over the initiation and termination steps during the course of polymerization, and this polymerization is a much cleaner reaction than chemical oxidation, as it does not require any additional chemicals.⁷³

The electrochemical polymerization of aniline is carried out using a two-electrode system where the electrodes are dipped in the electrolytic solution of monomer. A specific current (in the case of constant current) is passed through the solution, which results in the formation of a polyaniline film on the surface of the electrode. At constant potential, aniline is polymerized in the form of powder, which is feebly deposited on the electrode. Usually, electro-oxidation of aniline is commonly carried out using inert electrodes such as Cu, Au, mild steel, graphite, etc.

1.4.3. Mechanism of Polymerization. The mechanism of oxidative polymerization of aniline is a chain reaction at a pH less than 2.5. This reaction basically proceeds through the chain growth mechanism by the addition of aniline monomers. The kinetic investigations reveal that the initial step is a slow phase due to the formation of a high molecular weight conducting polymer having a complex character.⁷⁴ The dimers are formed upon oxidation and react with aniline molecules through an electrophilic aromatic substitution reaction, forming trimers and tetramers. This process is continuously repeated until a monomer is present, which forms a polyaniline.

The general mechanism for the polymerization of aniline proceeds through the following steps, irrespective of chemical or electrochemical techniques.

1.4.3.1. Initiation. In this step, formation of a radical anilinium cation takes place via electron transfer to the aniline nitrogen atom (Figure 4). The anilinium radical cation undergoes various resonating structures and stabilizes itself.

1.4.3.2. Propagation. In the propagation step, a head-to-tail reaction takes place between the anilinium radical cation and its

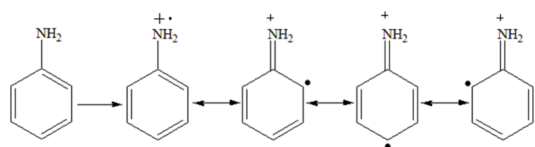


Figure 4. Mechanism for the formation of an anilinium radical cation.

resonance form in an acidic environment, resulting in a dimerization reaction. The dimers are immediately oxidized to form a dimerized radical cation as shown in Figure 5.

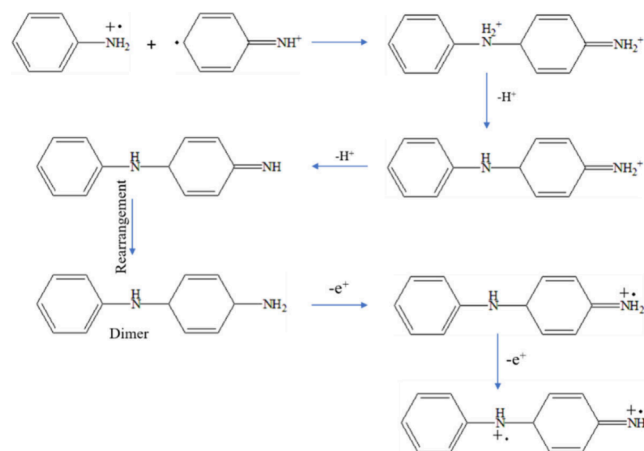


Figure 5. Mechanism for the formation of an anilinium cation dimer and the corresponding radical cation.

1.4.3.3. Formation of Polyaniline. In this termination step, the dimer radical reacts with an anilinium cation radical or dimer cation radical to form a trimer or tetramer through an electrophilic aromatic substitution reaction. The repetitions of these above steps lead to the formation of a polyaniline chain (Figure 6).

2. ORGANIC TRANSFORMATIONS CATALYZED USING POLYANILINE-SUPPORTED CATALYST

The polyaniline-supported catalyst was used as an efficient, inexpensive, and nontoxic catalyst for many organic transformations, such as Mannich-type reactions, esterification reactions, aza-Michael reactions, Suzuki–Miyaura couplings, Heck reactions, acylation reactions, and many more transformation reactions (miscellaneous reactions), which are described.

2.1. Mannich-type Reaction. The Mannich reaction is one of the most important chemical reactions in organic synthesis for synthesizing β -amino carbonyl compounds. The Mannich reaction is a reaction of aliphatic/aromatic aldehydes, amines, and ketones under acid/base conditions, providing Mannich base/ β -amino carbonyl compounds or derivatives (Scheme 1). β -Amino carbonyl compounds are extensively used as biologically active compounds and intermediates in many natural products. Further, β -amino carbonyl compound derivatives have many applications in various therapeutic agents, such as anticancer, anti-inflammatory, antimicrobial, and anticonvulsant agents, among others (Figure 7).

Palaniappan et al. investigated modified polyaniline with different acids such as Brønsted acids (H_2SO_4 , HCl, HClO_4 , and HBF_4), organic acids (5-sulfosalicylic acid (SSA), *p*-toluene sulfonic acid (PTSA)), and Lewis acids (InI_2 and FeCl_3) (Scheme 2).⁷⁵ They showed the catalytic activities of these polyaniline salts and complexes for the synthesis of β -amino carbonyl compounds through a Mannich-type reaction under solvent-free conditions. Out of the different catalysts reported by this group, the highest yield was obtained at 86% of the product when aniline, benzaldehyde, and cyclohexanone were subjected to the reaction under solvent-free conditions at 30 °C for 6 h. They also showed the diastereoselectivity of some β -amino

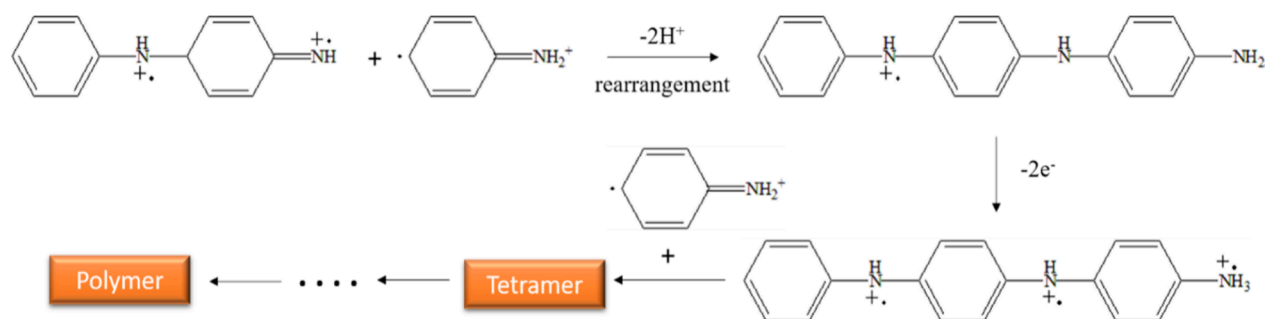


Figure 6. Plausible mechanism for polyaniline formation.

Scheme 1. Synthesis of β -Aminocarbonyl Compound Derivatives

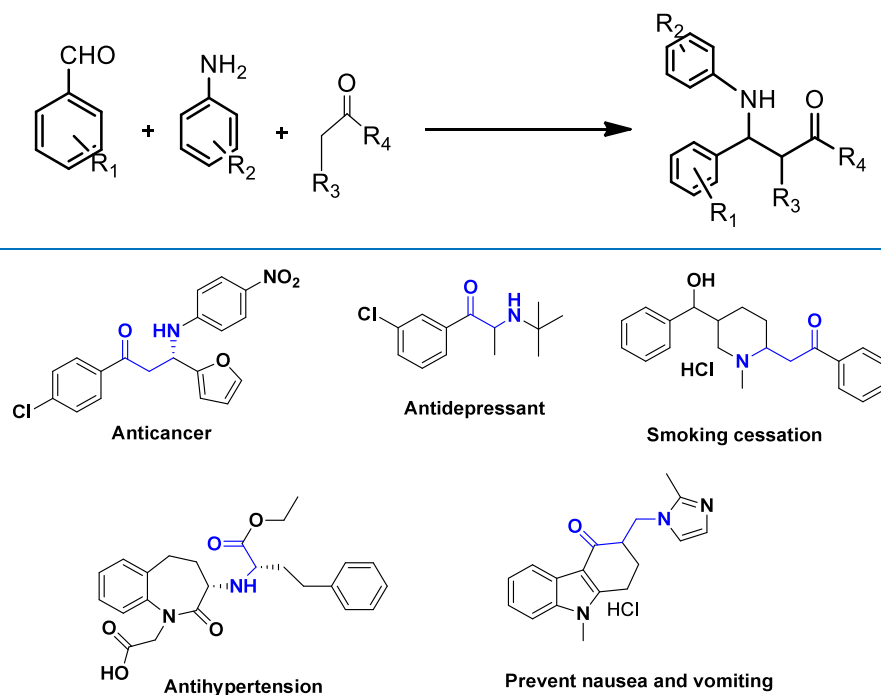
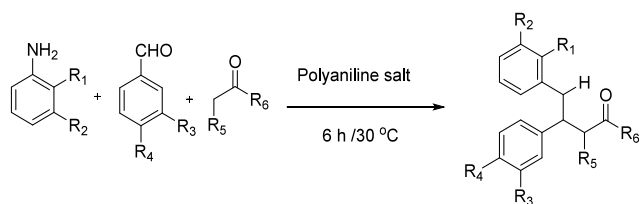


Figure 7. Some useful and important β -amino carbonyl compounds.

Scheme 2. Synthesis of β -Amino Carbonyl Compounds by Polyaniline Salts

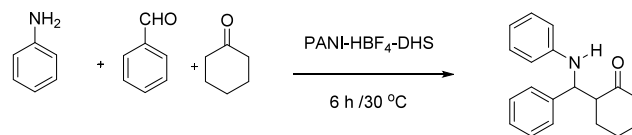


carbonyl compounds and claimed these catalysts are feasible due to their easy synthesis, eco-friendliness, stability, and reusability.

Palaniappan et al. also reported polyaniline–fluoroboric acid–dodecylhydrogensulfate salt for Mannich reaction of aromatic aldehydes, amines, and cyclohexanone in 2005 (Scheme 3).⁷⁶ They showed that using 25 wt % PANI-HBF₄-DHS salt catalyst produced an 80% yield of the product in 6 h at 30 °C without the need for a solvent.

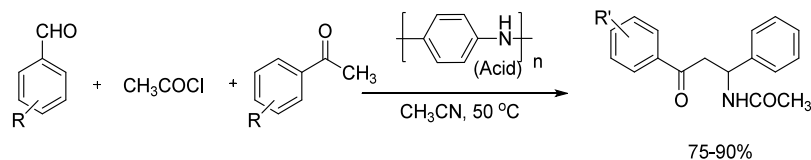
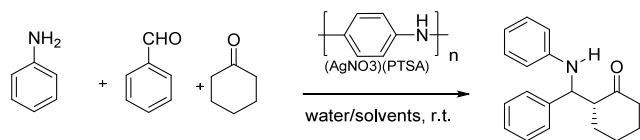
Nabid and group reported a one-pot synthesis of β -acetamido ketones via a four-component condensation reaction using polyaniline-supported acid catalysts (Scheme 4).⁷⁷ The used

Scheme 3. Mannich Reaction Catalyzed by Polyaniline–Fluoroboric Acid–Dodecylhydrogensulfate Salt



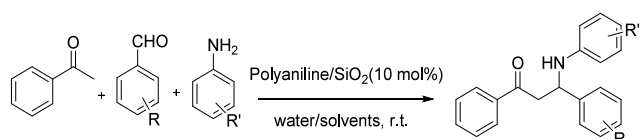
polyaniline-supported acid catalysts are polyaniline-hydrochloride, polyaniline-sulfate, and polyaniline-nitrate. Using aniline, acetophenone, and acetyl chloride in the presence of 20 wt % polyaniline-sulfate catalyst at 50 °C for 60 min produced the highest yield (90%) among other reactants. The catalyst can be reused multiple times without the loss of its catalytic activity.

In the year 2010, Palaniappan and group reported the modification of polyaniline with dual dopants, silver nitrate and *para*-toluene sulfonic acid (PANI-AgNO₃-PTSA), and the modified compound was used as a catalyst for the one-pot synthesis of β -amino ketones in water medium with stereoselectivity (Scheme 5).⁷⁸ The group showed that the reaction of benzaldehyde, aniline, and cyclohexanone in the presence of PANI-AgNO₃-PTSA catalyst was carried at room temperature

Scheme 4. One-Pot Synthesis of β -Acetamido Ketones by Polyaniline-Supported CatalystsScheme 5. One-Pot Synthesis of β -Acetamido Ketones by Polyaniline-Supported Catalysts

for 70 min, which produced the highest yield (96%) in a water medium with 100% *anti*-isomers.

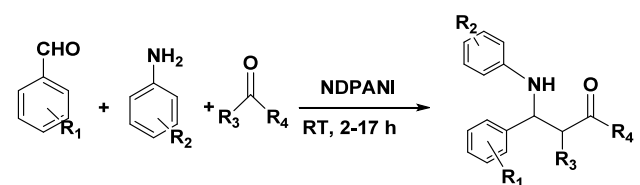
Yelwande et al. modified polyaniline with SiO₂ and used the product as a catalyst for synthesis β -amino carbonyl compounds via one-pot Mannich reactions employing acetophenone, aromatic aldehyde, and aromatic amines (Scheme 6).⁷⁹ This

Scheme 6. Mannich Reaction Using a Polyaniline/SiO₂ Catalyst

method produces the highest yield (93%) of product when subjected to benzaldehyde, aniline, and acetophenone within 3 h in presence 0.1 g of catalyst under an ethanol medium. The authors claimed this method provides the following advantages: noncorrosive, nontoxic, and inexpensive reaction conditions. The catalyst was recovered and reused.

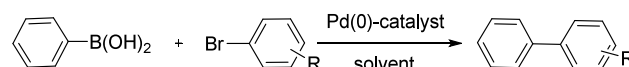
In 2021, our group (Behera et al.) doped potash alum, a nontoxic substance, on the nanopolyaniline chain and used this alum-doped nanopolyaniline (NDPANI) for the synthesis of β -amino carbonyl compounds via a Mannich reaction under solvent-free conditions at room temperature. An excellent yield of the product was obtained within a short period of time (Scheme 7).⁸⁰ The highest yield was obtained at 95% when 4-methoxy benzaldehyde, aniline, and acetone were allowed to react under solvent-free conditions.

2.2. Suzuki–Miyaura couplings. Suzuki–Miyaura coupling is one of the most important and frequently used reactions in many organic syntheses for the formation of C–C bonds. It is typically a cross coupling between organoboronic acid and aryl halides in the presence of palladium(0)-based catalysts (Scheme

Scheme 7. One-Pot Synthesis of β -Amino Carbonyl Compounds Catalyzed by NDPANI

8). A recent development revealed that it is not confined to only aryls but instead extended to alkyl, alkenyls and alkynyls. Also,

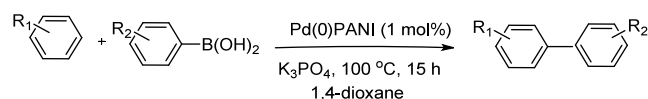
Scheme 8. General Representation of Suzuki–Miyaura Coupling



instead of boronic acids, organoboranes, boronate esters, or potassium trifluoroborates may be used.

Houdayer et al. synthesized polyaniline-supported Pd(0) via a one-pot chemical route having a particle size on the nanoscale (Scheme 9).⁸¹ They used polyaniline-supported Pd(0) nano-

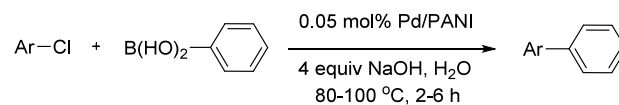
Scheme 9. Polyaniline-Supported Pd(0) for Suzuki–Miyaura Reactions



composite as a heterogeneous catalyst for Heck and Suzuki–Miyaura reactions of aryl iodides with excellent yield. The notable highest obtained yields were 89% and 83% for the Heck and Suzuki–Miyaura reactions, respectively.

Gallon et al. synthesized palladium nanoparticles supported on polyaniline nanofibers and used them as semiheterogeneous catalysts in water for organic transformation (Scheme 10).⁸²

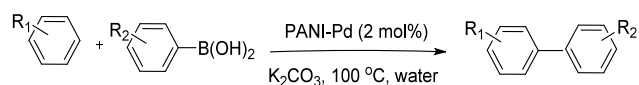
Scheme 10. Suzuki–Miyaura Reaction Catalyzed by Palladium Nanoparticles Supported on Polyaniline Nanofibers



The catalytic activity of palladium nanoparticles supported on polyaniline was investigated in the Suzuki coupling reaction of aryl halides and phenyl boronic acids in water. In this methodology, when 4-acetylphenyl chloride was allowed to react with phenylboronic acid in the presence of 0.05 mol % catalyst, which produced 91% yield of product, and the reusability of the catalyst was shown by the 89% yield obtained even after 10 cycles. This group claimed that all the products obtained had a higher yield.

Kantam et al. developed a polyaniline-supported palladium catalyst by using different palladium precursors for the Suzuki–Miyaura coupling of bromo- and chloroarenes with aryl boronic acids in water (Scheme 11).⁸³ In this methodology, the highest obtained yield was 99% when 4-bromobenzaldehyde was allowed to react with phenyl boronic acid in the presence of K₂CO₃ (3 mmol) and 2 mol % PA–Pd₄ catalyst in water at 100 °C within 45 min under N₂ atmosphere. They found that the

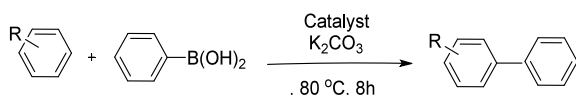
Scheme 11. Suzuki–Miyaura Reaction of Bromo- and Chloroarenes with Arylboronic Acids



catalyst prepared from PdCl₂ is best in terms of activity, and the catalyst can be easily recovered and reused for several cycles.

Islam et al. reported a Suzuki reaction between derivatives of benzene bromide and phenylboronic acid using a palladium-polyaniline hybrid catalyst and observed the excellent yield with high TOF values (Scheme 12).⁸⁴ The palladium-polyaniline

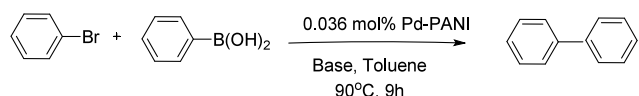
Scheme 12. Suzuki Reaction Catalyzed by Palladium-Polyaniline Hybrid Catalyst



nanocomposite material was synthesized using an in situ technique in which palladium acetate and aniline hydrochloride were used as the precursors of the composite. The authors claimed that when 4-nitro benzene bromide was allowed to react with phenylboronic acid in the presence of K₂CO₃ and 0.02 mol % catalyst in toluene at 80 °C for 8 h, the highest yield (99%) of the product was obtained with a TOF of 1732 h⁻¹ as compared to another substrate.

Siril and group developed a polyaniline palladium nanocomposite catalyst for green Suzuki–Miyaura coupling reactions (Scheme 13).⁸⁵ This method showed that the Suzuki–Miyaura

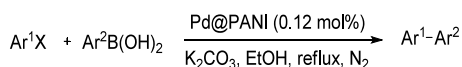
Scheme 13. Suzuki–Miyaura Reaction Catalyzed by Polyaniline Palladium Nanocomposite Catalyst



reaction proceeds much faster in water than in toluene. The excellent catalytic activity of the nanocomposite resulted in 86% and 91% yields of product in water and toluene, respectively, when potassium carbonate was used as the base.

Yu et al. reported the modified polyaniline prepared using palladium nanoparticles for the Suzuki cross-coupling reaction (Scheme 14).⁸⁶ The catalyst is directly used for the Suzuki

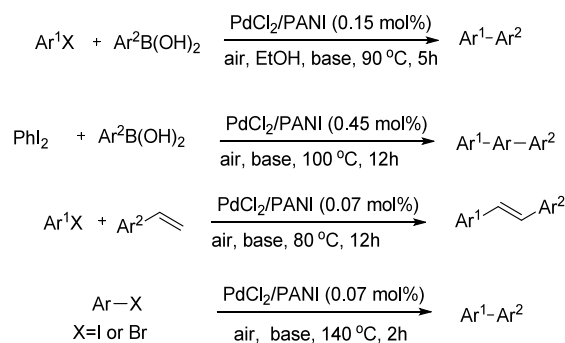
Scheme 14. Suzuki Cross-Coupling Reaction Catalyzed by Palladium Nanoparticles



reaction without baking, additional ligands, or organic bases. This coupling with high catalytic activity required a very small amount of catalyst (0.12 mol %). The catalyst is cheap, reusable, and highly stable (tested for 1 year under normal conditions).

Wang et al. reported a divalent palladium/zero palladium-doped polyaniline network and used it as an excellent nanocatalyst for C–C coupling reactions (Scheme 15).⁸⁷ They showed C–C coupling reactions through Ullmann and Suzuki coupling reactions. The catalyst exhibits excellent

Scheme 15. Suzuki Cross-Coupling Catalyzed by Polyaniline/Palladium Catalyst

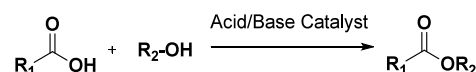


catalytic performance in various C–C coupling reactions. The catalyst can be regenerated easily and reused more than 8 times.

2.3. Esterification Reactions. The esterification reaction is an important organic transformations, as it provides useful ester compounds. Esters are found naturally, as well as synthetically. In organic synthesis, esters are the most common compounds and are most widely used in many applications such as natural products, pharmaceuticals, main components of diesel, polymers, paints, agrochemicals, fragrances, and many more. Esters are also used as solvents such as ethyl acetate and methyl acetate. In day-to-day life, esters are frequently used as food flavorings and preservatives.

The synthesis of esters is a typical reaction of carboxylic acid with alcohols in the presence of an acid or base catalyst and is known as an esterification reaction (Scheme 16). To date, many

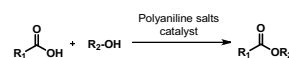
Scheme 16. General Representation of an Esterification Reaction



catalysts have been developed, many of which have advantages as well as disadvantages. Here we discuss polyaniline-supported catalysts for esterification reactions and their advantages over other catalysts.

Palaniappan et al. developed polyaniline salts using hydrochloride, sulfate, nitrate, phosphate, and *p*-toluene sulfonate and studied the catalytic activities in the esterification of a carboxylic acid with alcohols (Scheme 17(a)).⁸⁸ When lauric acid was

Scheme 17. General Esterification Reaction Catalyzed by (a) Polyaniline/Hydrochloride, Sulfate, Nitrate, Phosphate, and *p*-Toluenesulfonate, (b) MSA-PANI, CSA-PANI, and LG-PANI, or (c) SiO₂-pani-MSA



Dopant:
a) hydrochloride, sulfate, nitrate, phosphate and *p*-toluenesulphonate
b) methanesulfonic (MSA-PANI), camphorsulfonic (CSA-PANI) and lignosulfonic (LG-PANI)
c) methanesulfonic or methanesulfonic acid

allowed to react with methanol under solvent-free conditions using different polyaniline catalysts such as polyaniline hydrochloride, sulfate, nitrate, phosphate, and *p*-toluene sulfonate, it produced high yields of 99%, 99%, 99%, 75%, and 99% respectively. The authors claimed this proposed method is easy,

environmentally friendly, and effective for ester product formations and that the catalysts that can be reused.

The polyaniline was oxidized using benzoyl peroxide in the presence of sulfuric acid and sodium lauryl sulfate surfactant, and the resulting salt was used as a catalyst for the esterification reaction reported by Ram et al.⁸⁹ The group took different carboxylic acids with methanol, out of which lauric acid produced highest yield at 90 °C within 24 h. They claimed the mechanism of the reaction would be similar to the pyridinium *p*-toluenesulfonate-catalyzed esterification reaction.

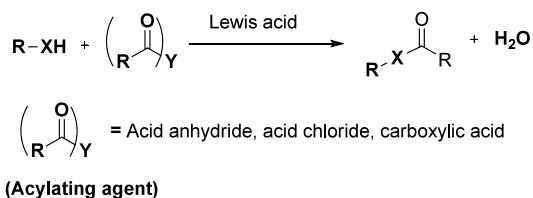
Drelinkiewicz et al. reported the use of some polyaniline-supported organo-sulfonic acids such as methanesulfonic (MSA-PANI), camphorosulfonic (CSA-PANI), and lignosulfonic (LG-PANI) acid as catalysts for the esterification of fatty acid (ricinoleic) with methanol (Scheme 17(b)).⁹⁰ Out of the three developed catalysts, MSA- and CSA-doped polyanilines exhibited high catalytic activity and good stability in the reaction mixture.

Kalamba-Jaje et al. developed polyaniline-doped methanesulfonic or methanesulfonic acid, which are deposited on silica and carbon (Scheme 17(c)).⁹¹ The catalytic activity of doped polyaniline was explored in the esterification of ricinolein acid with methanol at 55 °C. Among both the catalysts, silica coated with methanesulfonic acid polyaniline (SiO₂-pani-MSA) exhibits the highest catalytic activity.

Amarnath et al. explored the esterification of phenylacetic acid with methanol using polyaniline salts, which were synthesized by oxidative polymerization using benzoyl peroxide as an oxidizing agent.⁹² The polyaniline salt catalyst provides good to excellent yields, and the catalyst can be recovered and reused many times.

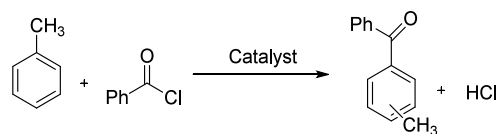
2.4. Acylation Reactions. Acylation reactions are one of the best ways to protect alcohols, amines, and thiols. Generally, for acylation reactions, acid anhydrides, acid chlorides, and carboxylic acids are used as acylating agents. The acylated products, such as esters and amides, are widely used in pharmaceuticals, polymers, medicinal compounds, and solvents. Generally, the acylation reaction is catalyzed by Lewis acid catalysts, but it has some limitations, such as the fact that during workup time the Lewis acid catalyst is destroyed when acetic acid is used as an acylating agent (Scheme 18). Many catalysts have been developed and used for acylation, solving many limitations of traditional methods.

Scheme 18. General Acylation Reaction Catalyzed by Lewis Acid



Rezaei et al. developed polyaniline-supported ZnO nanoparticles and explored their catalytic activity in Friedel–Crafts acylation reactions as heterogeneous catalysts (Scheme 19).⁹³ In this methodology, the Friedel–Crafts acylation reaction between toluene and benzyl chloride in the presence of 20 mol % catalyst at a temperature of 40 °C under solvent-free conditions produced the highest yield (93%). However, the same yield was obtained by increasing the amount of catalyst (30%) at room temperature. This catalyst provides an excellent

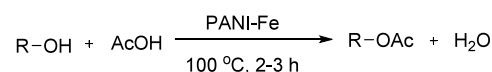
Scheme 19. Polyaniline-Supported ZnO Nanoparticle-Catalyzed Friedel–Crafts Acylation Reaction



yield and shows high thermal stability (up to 500 °C) and reusability.

Likhar et al. developed a reusable polyaniline nanofiber-supported FeCl₃ (PANIn-Fe) heterogeneous catalyst and showed its catalytic activity in the acylation of alcohols and amines with acetic acid as the acylating agent (Scheme 20).⁹⁴ All

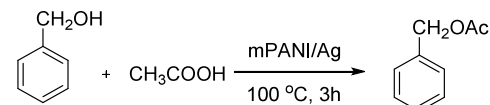
Scheme 20. Acylation of Alcohols and Amines with Acetic Acid by PANIn-Fe



the reactions were allowed under solvent-free conditions in the presence of 25 mg of catalyst at a temperature of 110 °C and produced excellent yields (56–92%, acylation of alcohol). This catalyst has selectivity between OH and NH₂ groups. In case of 2-aminophenol and 4-aminophenol, only the amine group was selectively acylated.

Mandi's group designed a mesoporous polyaniline-supported silver nanoparticle catalyst (mPANI/Ag) and studied the catalytic activity and reusability for the acylation of alcohols and amines under solvent-free conditions at 140 °C (Scheme 21).⁹⁵ They claimed this catalytic method was green and found

Scheme 21. Acylation of Alcohols and Amines with Acetic Acid by mPANI/Ag

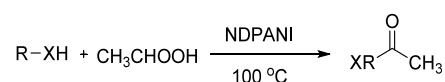


that a minimum of 25 mg of catalyst was required for better yield. The excellent product yield was obtained under optimized conditions for the acylation of alcohol (48–98%) and amines (62–98%) yields.

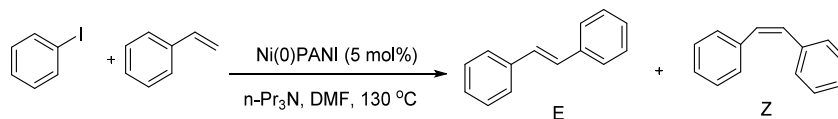
Lee et al. reported using nanoporous polyaniline emeraldine salts as catalysts for the easy and effective acylation and oxidation of primary amines and alcohols into amide/ester or aldehyde compounds.⁹⁶ This methodology is environmentally benign and safe, operationally simple, and highly chemoselective.

Recently, our group (Behera et al.) described an efficient, economical, and ecofriendly acylation of alcohols and amines by alum-doped nano polyaniline (NDPANI) under solvent-free conditions at 100 °C. This catalyst was synthesized by the oxidative polymerization of aniline with APS as an oxidant (Scheme 22).⁹⁷ This method provides excellent yields of the

Scheme 22. NDPANI-Catalyzed Acylation of Alcohols and Amines with Acetic Acid



Scheme 23. Heck Reaction Coupling between Aryl Iodides and Olefins Catalyzed by Polyaniline Nickel(0) Nanocomposites



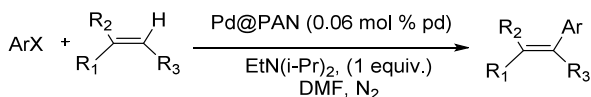
products (77–95%) with high purity, and the authors claim that this catalyst is nonhazardous, cheap, reusable, and easy to prepare and handle.

2.5. Heck Reactions. Heck reactions are generally reactions of unsaturated halides with alkenes in the presence of a metal catalyst and a base. Traditionally, the Pd metal catalyst is used as a suitable catalyst for Heck reactions. In recent times, many catalysts have been developed, with many advantages. Here, we describe the following schemes based on polyaniline-supported metal catalysts for Heck reactions.

Houdayer et al. developed polyaniline nickel(0) nanocomposites and used these materials to catalyze Heck reactions (Scheme 23).⁹⁸ They compared the reactivity of polyaniline nickel(0) nanocomposites with that of nickel catalysts in Heck coupling between aryl iodides and olefins and observed the reaction is faster in the case of the nanocomposites compared to the nickel catalysts. In this approach, 3-iodoanisole couples efficiently with methyl acrylate to selectively produce the *E*-olefin product (one isomer by GC/MS and ¹H NMR) in an 81% yield. The product was separated as an isomer mixture when the reaction was carried out using *n*-butyl acrylate (*E/Z* = 80:20).

Yu et al. doped polyaniline with Pd nanoparticles using air as the oxidant instead of traditional persulfates and used the derivative as a catalyst for Heck reactions with a wide substrate scope (Scheme 24).⁹⁹ The reaction was carried out under DMF

Scheme 24. Heck Reactions Catalyzed by Polyaniline Doped with Pd Nanoparticles

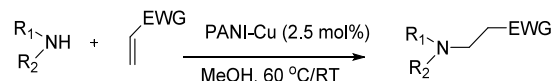


solvent in the presence of 0.06 mol % catalyst at 120 °C, which provided the highest yield of products (99%). They found that the Pd@PANI catalyst is heterogeneous, accessible, practical, and stable and might be developed to be a reliable alternative catalyst to the traditionally employed palladium complexes.

2.6. Aza-Michael Reaction. The aza-Michael reaction is a simple and attractive strategy for the synthesis of nitrogen-containing C–N compounds such as β -amino carbonyl compounds, nitrile compounds, etc. Compounds containing a carbon–nitrogen bond are very important for the synthesis of biological active molecules and pharmaceutical compounds.¹⁰¹ Below, we summarize polyaniline-supported catalysts for the aza-Michael reaction.

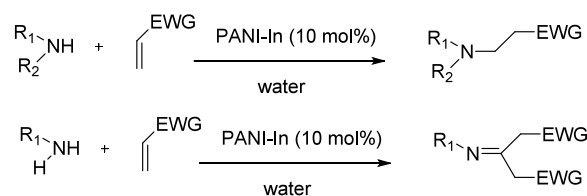
Kantam et al. developed polyaniline-supported CuI and used this catalyst for C–N bond formation through the *N*-arylation of *N*(H)-heterocycles and benzyl amines with aryl halides and aryl boronic acids, as well as aza-Michael reactions of amines with activated alkenes. In this methodology, amines reacted with alkenes at 60 °C under methanol in the presence of 2.5 mol % catalyst, which provided the products in excellent yields (60–98%) (Scheme 25).¹⁰⁰ Moreover, the catalyst was recovered easily and reused several times.

Scheme 25. Aza-Michael Reaction Catalyzed by Polyaniline-Supported CuI



Likhar et al. reported organic transformations, such as the Suzuki–Miyaura reaction, acylation, the Heck reaction, the aza-Michael reaction, and *O*-arylation of phenol with aryl-chlorides, using a synthesized polyaniline-supported palladium catalyst (Scheme 26).¹⁰¹ This methodology successfully catalyzed all the

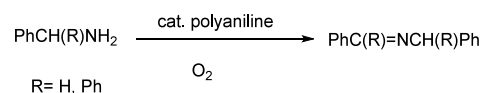
Scheme 26. Aza-Michael Reaction Catalyzed by a Polyaniline-Supported Palladium Catalyst



reactions in the presence of 10 mol % PANI-In catalyst under water as a solvent, providing excellent yields of the products (66–95%) within short periods.

2.7. Miscellaneous Organic Transformations. Early in the year 1993, Hirao et al. reported the dehydrogenative oxidation or decarboxylative oxidation of benzyl amines and 2-phenylalanine into corresponding imines in the presence of polyaniline as a catalyst (9.1 mg) with a combination of iron(II) chloride or copper(II) chloride in different solvents at 80 °C.¹⁰² This methodology provides good to excellent yields of products (Scheme 27). On the other side, cinnamyl alcohol is converted into cinnamaldehyde, possibly due to complexation.

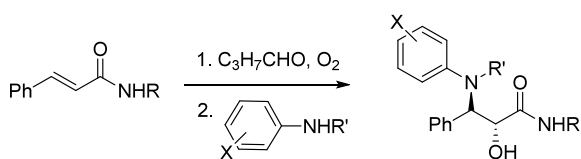
Scheme 27. Decarboxylative Oxidation Catalyzed by a Polyaniline Catalyst



Das et al. designed a polyaniline-supported cobalt(II) salen catalyst for the one-pot synthesis of β -phenylisoserine derivatives from cinnamoyl amide by the formation of epoxide followed by opening with aniline at ambient conditions (Scheme 28).¹⁰³ This reaction procedure provides good to excellent yields of products (>90% purity), and the stereochemistry of the synthesized amides is *anti* in all cases. However, the ¹H NMR of the crude reaction mixture revealed the existence of a minor (15%) amount of the corresponding *syn* diastereomer. The authors claimed this catalyst is an extremely versatile catalyst for the synthesis of β -phenylisoserine.

Prabhakaran et al. also used a polyaniline-supported cobalt(II) salen catalyst for the π -facially selective aerobic epoxidation (oxygen–2-methylpropanal) of *N*-cinnamoyl proline-derived

Scheme 28. One-Pot Synthesis of β -Phenylisoserine Derivatives by Polyaniline-Supported Cobalt



peptides.¹⁰⁴ (Scheme 29) The reported methodology provided 80–90% isolated yields of the epoxides in all cases, and the ratio of diastereomers was determined by HPLC, with the absolute configuration of 2*R*,3*S*. The authors observed the diastereoselectivity for the peptides and that they adopt a γ - or β -turn due to intramolecular hydrogen bonding.

Palaniappan and group used polyaniline salts as catalysts for the tetrahydropyranlation of decanol (Scheme 30).¹⁰⁵ They used benzoyl peroxide for the oxidation of aniline to polyaniline in the presence of protic acids.

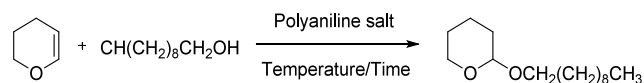
Polyaniline salts have been used as catalysts for the tetrahydropyranlation of alcohols in a process reported by Palaniappan et al. for the first time (Scheme 31).¹⁰⁶ The group reported the tetrahydropyranlation of behenyl alcohol using different polyaniline salts such as polyaniline sulfate, polyaniline nitrate, and polyaniline hydrochloride, which produced 78%, 50%, and 47% yields of the product, respectively. An optimized 20 wt % polyaniline sulfate catalyst was used for the tetrahydropyranlation of different alcohols at 50 °C temperature, and the reaction mixture was allowed to stir for 8 h to give good to excellent yields. The catalytic use of polyaniline salts is practical because of their easy preparation, recovery, and reusability.

Handique et al. reported polyaniline-supported copper(II) and *cis*-bisglycinato copper(II) monohydrate catalysts for the oxidation of aldimines, aldoximes, and aldehydes to the corresponding carboxylic acids with excellent yields (72–100%) at 60 °C within 2–6 h (Scheme 32).¹⁰⁷ The mechanism involved an oxy radical method, which was confirmed by ESR.

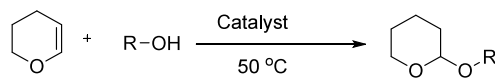
Kowalski et al. proposed different conjugated polymer-based (polyaniline, poly-*o*-toluidine or poly-*o*-anisidine) cobalt catalysts (Scheme 33).¹⁰⁸ They used these catalysts for the oxidation of alkenes at atmospheric pressure in the presence of molecular oxygen. Alkenes with terminal double bonds have low reactivity; therefore, they require longer reaction times. Catalysts based on cobalt acetate need less time to obtain satisfactory yields. Oxidation of double bonds proceeds more easily when the double bond is activated by the presence of another group. The product epoxides or ketones were obtained with high selectivity and yields under acetonitrile medium at 20 °C temperature.

Athawale et al. reported a polyaniline nanocomposite containing copper nanoclusters synthesized by using oxidative polymerization with ammonium persulfate as an oxidant.¹⁰⁹ The material was well characterized by different methods and used

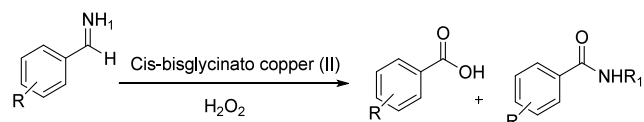
Scheme 30. Polyaniline Salt-Catalyzed Tetrahydropyranlation of Decanol



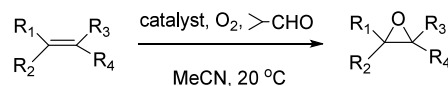
Scheme 31. Polyaniline Salt-Catalyzed Tetrahydropyranlation of Alcohols



Scheme 32. Oxidation of Aldimines, Aldoximes, and Aldehydes by a Polyaniline Catalyst



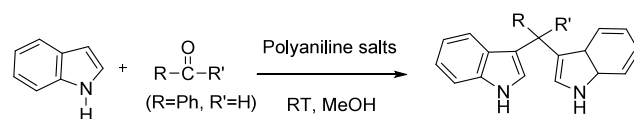
Scheme 33. Oxidation of Alkenes by a Substituted Polyaniline-Supported Cobalt Catalyst



for Wacker oxidation of 1-decene to 2-decanone in the presence of molecular oxygen under a water–acetonitrile system at 50–60 °C.

Palaniappan et al. reported the doping of polyaniline base with different Brønsted acids (H₂SO₄, HNO₃, and H₃PO₄), organic acid *p*-toluene sulfonic acid (PTSA), and iodine (I₂) (Scheme 34). They also prepared polyaniline complexes with Lewis acids

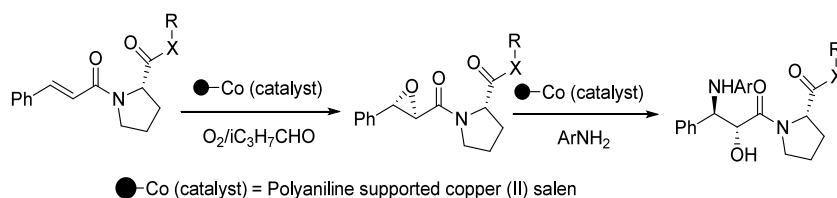
Scheme 34. Synthesis of Bis-Indole by Polyaniline-Doped Acids



(BF₃, AlCl₃, and SnCl₂).¹¹⁰ All of the catalysts were well characterized and used for the synthesis of bisindole for the first time. The group claimed that using the PANI-H₂SO₄ catalyst, the synthesis of bisindole in methanol at room temperature provides excellent yields (98–99%) with an environmentally benign method.

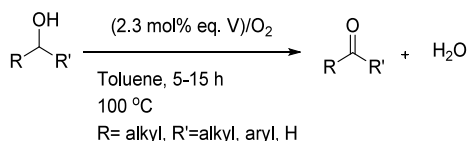
Reddy and the group reported that polyaniline was modified with vanadium complexes and explored the catalytic activity in the aerobic oxidation of alcohols to aldehydes and ketones (Scheme 35).¹¹¹ The resulting aldehydes were obtained at 100

Scheme 29. π -Facially Selective Aerobic Epoxidation by Polyaniline-Supported Cobalt



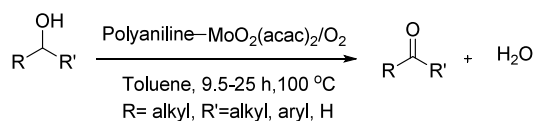
°C in toluene within 5–15 h and provided the products in excellent yields (72–99%).

Scheme 35. Aerobic Oxidation of Alcohols Using Polyaniline Vanadium Catalyst



Polyaniline was modified using a molybdenum complex and used as a catalyst for the oxidation of alcohols to aldehydes and ketones in toluene at 100 °C, which was reported by Velusamy et al. (Scheme 36).¹¹² The oxidation occurs in the presence of

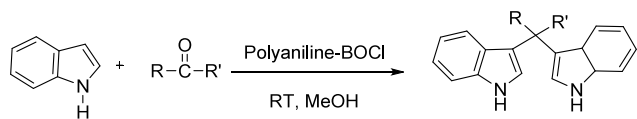
Scheme 36. Oxidation of Alcohols Using a Polyaniline Molybdenum Catalyst



molecular oxygen with constant stirring, which provides high yields of products (52–98%) within 9.5–25 h. The authors revealed that primary alcohols react more quickly than secondary ones. The catalyst can be recovered and reused without losing its catalytic activity.

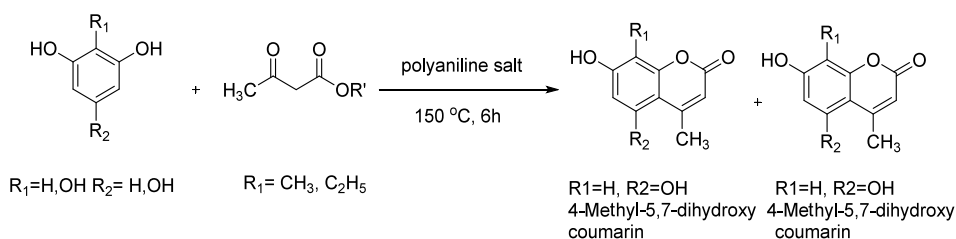
Palaniappan et al. also synthesized a polyaniline bismoclite composite and employed it as a catalyst for the condensation of indole with carbonyl compounds for the synthesis of bis(indolyl)methanes in excellent yields (52–99%; Scheme 37).¹¹³

Scheme 37. Polyaniline Bismoclite Composite-Catalyzed Synthesis of Bis(indolyl)methanes



The following year, Palaniappan's group reported a polymer-supported acid catalyst (polyaniline-sulfate salt) that used as a powerful catalyst for the transformation of phenolic compounds and β -keto esters into coumarin derivatives by a thermal heating process (Scheme 38).¹¹⁴ The polyaniline-supported sulfuric acid catalyst provides various advantages, including ease of manufacture, activity, recovery, recyclability, lack of solvent, high yield, and environmental friendliness.

Scheme 38. Polyaniline-Sulfate Salt-Catalyzed Synthesis of Phenolic Compounds and Coumarin Derivatives



Gangadasu et al. reported different types of polyaniline salts by doping a polyaniline base with different Brønsted acids (sulfuric, nitric, phosphoric, perchloric, and hydrochloric acid) and organic acids (*p*-toluene sulfonic acid and 5-sulfosalicylic acid) as well as Lewis acids (aluminum chloride and ferric chloride) (Scheme 39).¹¹⁵ They explored the catalytic activities of those catalysts in a Biginelli reaction for synthesis of 5-(methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one at 64 °C. Among these catalysts, polyaniline-*p*-toluene sulfonate salt (5 wt %) showed better catalytic performance for the product formation with excellent yields (97–98%) within 2 h.

Blaz et al. developed cobalt complexes with conjugated polymers such as polyaniline (PANI), poly-*o*-toluidine (POT), and poly-*o*-anisidine (POA) as supports (Scheme 40).¹¹⁶ They used these complexes as catalyst for the oxidation of aliphatic and aromatic hydrocarbons in the presence of molecular oxygen at atmospheric pressure. The obtained epoxides or ketones had high selectivity. Alkene oxidation reactions were carried out by refluxing and stirring the reagents in acetonitrile in a glass reactor thermostated at 65 °C, providing excellent product yields.

John and group reported the synthesis of 1,8-dioxododecahydroanthene derivatives by the condensation of aryl aldehyde and 1,3-cyclohexanedione using 25 wt % (with respect to aldehyde) polyaniline-*p*-toluenesulfonate salt as a catalyst in water medium for 6 h, which provided 73–84% yields (Scheme 41).¹¹⁷

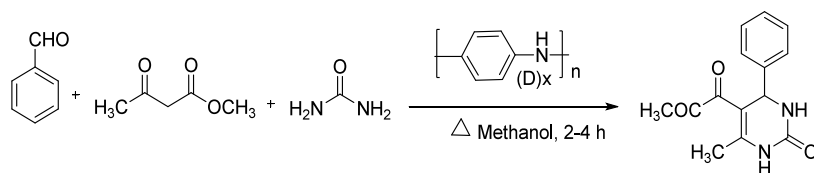
He and group reported the cycloaddition of CO₂ to epoxides catalyzed by polyaniline salts (Scheme 42).¹¹⁸ They synthesized polyaniline salts using different hydrogen halides (HX, X = I, Br, Cl) and used these catalysts for the cycloaddition of CO₂ to propylene oxide (PO) to produce propylene carbonate (PC). They found that PANI-HI was the most active and selective. By using PANI-HI, they also successfully reacted CO₂ with epichlorohydrin, and the optimized temperature was 115 °C with 5 MPa pressure. The catalytic activity of PANI-HCl is much lower than those of PANI-HI and PANI-HBr.

Srinivas and co-worker reported polyaniline-sulfate salt as an excellent catalyst for the synthesis of benzodiazepines and 2-phenyl benzimidazoles using the reaction of phenylenediamine with cyclic or acyclic ketones or aromatic aldehydes (Scheme 43).¹¹⁹ The group reported that 25 wt % optimized catalyst is sufficient to catalyze the reaction in dichloromethane solvent with excellent product yields (84–95%).

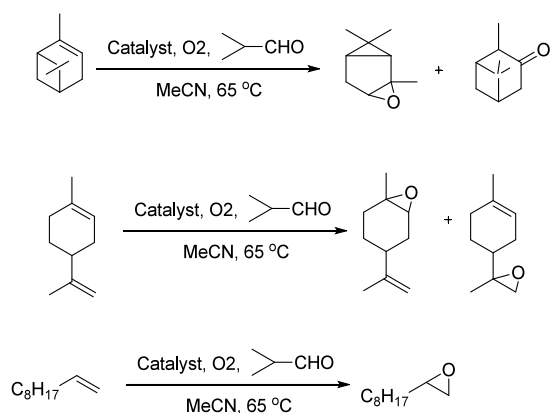
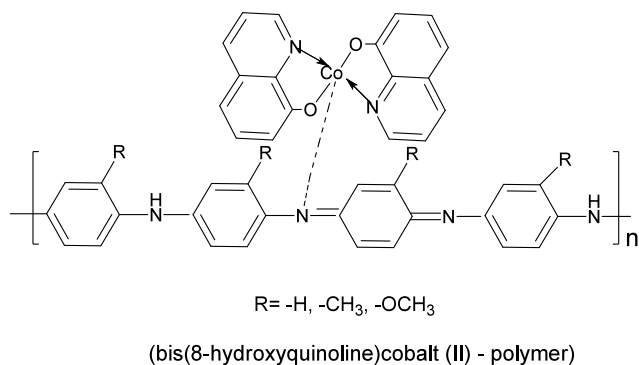
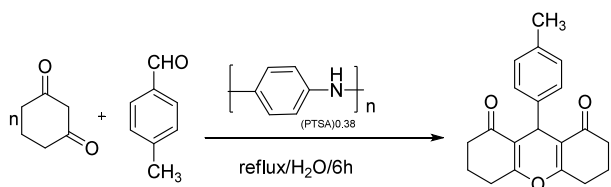
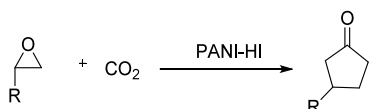
In 2007, Srinivas and team developed an efficient, conventional and reusable polyaniline-sulfate salt catalyst and explore its catalytic activities in the synthesis of quinoxaline derivatives.¹²⁰ (Scheme 44) The reaction proceeded smoothly with a 95–93% yield of products.

Kowalski et al. reported aerobic oxidation of alkenes using a polyaniline-supported cobalt catalyst. This catalyst showed efficient and selectivity for some unsaturated organic com-

Scheme 39. Polyaniline-Doped Acid Catalysts for the Biginelli Reaction

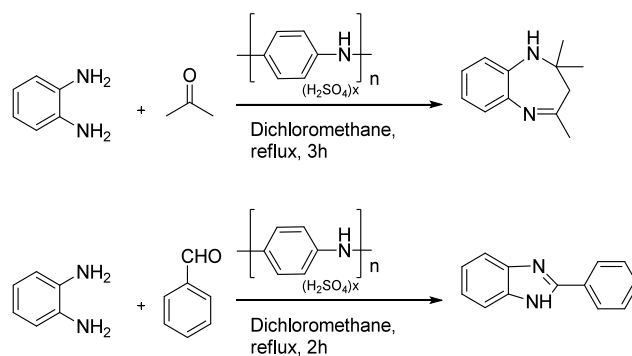


Scheme 40. Oxidation of Aliphatic and Aromatic Hydrocarbon

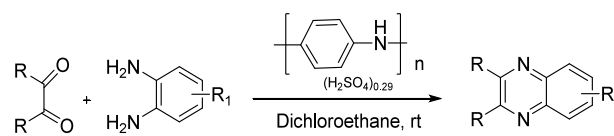
Scheme 41. Synthesized 1,8-Dioxo-dodecahydroanthene Derivatives by Polyaniline-*p*-toluenesulfonate SaltScheme 42. Cycloaddition of CO₂ with Epichlorohydrin by Polyaniline Hydrogen Halides

pounds.¹²¹ (Scheme 45) Oxidation of alkenes and cycloalkenes is carried out in the presence of 0.3 mol % catalyst at 60 °C under acetonitrile medium to give corresponding as a main product monoepoxy derivative.

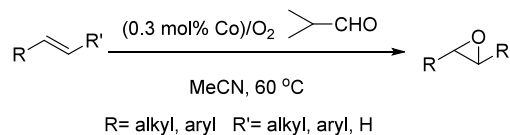
Scheme 43. Polyaniline-Sulfate Salt-Catalyzed Synthesis of Benzodiazepines and 2-Phenyl Benzimidazoles



Scheme 44. Synthesis of Quinoxaline Derivatives by Polyaniline-Sulfate Salt Catalyst



Scheme 45. Aerobic Oxidation of Alkenes Using a Polyaniline-Supported Cobalt Catalyst

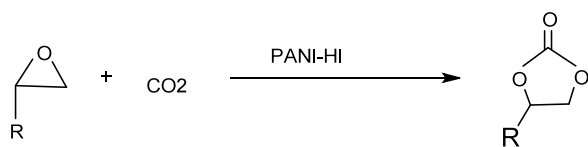


He et al. prepared Lewis acid-doped polyanilines by doping a polyaniline base with Lewis acids. They used them as catalysts for the first time for the acetalization of carbonyl compounds.¹²² The catalyzed acetalization of benzaldehyde with propane-1,2-diol proceeded in excellent yields with a simple and more environmentally benign procedure. The use of these doped Lewis acid catalysts is feasible because of their environmental friendliness, easy preparation, easy recovery, reusability, and good activity. This protocol provides high yields over a short reaction time. Further, the reusability of the catalyst has also been demonstrated.

The cycloaddition of CO₂ to epoxides using polyaniline salt catalysts (PANI-HCl, PANI-HI, and PANI-HBr) reported by He et al (Scheme 46).¹²³ The order of reaction activity of catalysts PANI-HI, PANI-HBr, and PANI-HCl was observed. The authors also revealed PANI-HI catalytic activity is sensitive below 115 °C. At this temperature, the yield of product increases with increases in the pressure of the gas.

Polyaniline was grafted with VO(acac)₂ and used as an effective catalyst for the synthesis of 5-diformylfuran from 5-hydroxymethylfurfural and fructose.¹²⁴ The oxidation provides excellent yields in methyl isobutyl ketone (MIBK), toluene, and

Scheme 46. Cycloaddition of CO₂ to Epoxides Using Polyaniline Salt Catalysts



4-chlorotoluene, having relatively lower polarity than other polar solvents. In the oxidation reaction, a high HMF conversion of 99.2% was obtained after 12 h at 110 °C, and DFF and 2,5-furandicarboxylic acid were obtained in yields of 86.2% and 11.7%, respectively.

Gao et al. synthesized polyaniline-supported palladium catalyst nanoparticles that showed catalytic activity in the hydrogenation of alkynes and cinnamaldehyde with high selectivity dominated by a kinetic mechanism (Scheme 47).¹²⁵ Moreover, they suggested that the variation in particle morphology resulting from substrates leads to differences in their catalytic efficiency, presumably due to the difference in surface area. With a catalyst loading of 5 mol %, the hydrogenation of ethyl phenylpropiolate achieves 100% conversion, similar to the PANI membrane-supported Pd. Cinnamaldehyde hydrogenation with a catalyst loading of 5 mol % is very selective for hydrocinnamaldehyde. The PANI-supported Pd nanoparticles are robust and can be reused at least seven times without significantly losing their catalytic activity and selectivity.

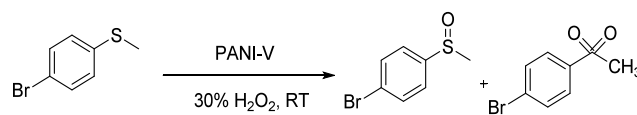
Lee et al. reported the oxidation of hydroquinone and primary/secondary alcohols to benzoquinone and aldehydes/ketones using a pernigraniline base catalyst.¹²⁶ The group compared catalytic activities of different polyaniline bases (emeraldine, leucoemeraldine, and pernigraniline) for oxidation alcohol under O₂/dioxane at 80 °C. However, pernigraniline provides a better yield (82%). The advantages of the catalyst are easy preparation, environmental friendliness, and chemo-selectivity.

Sreedhar and group reported the synthesis of polyaniline in the form of nanorods, nanospheres, and nanotubes (Scheme 48).¹²⁷ The group designed ammonium vanadate-doped polyaniline and studied its catalytic activity in sulfoxidation reactions H₂O₂ in water, with good to excellent yields of the products. Out of different shapes of nanopolyaniline, nanotubes and nanorods showed higher catalytic activity and selectivity than nanospheres. The catalyst can easily be recycled and reused.

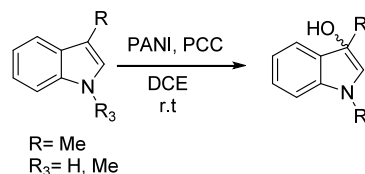
Kumar et al. used a combination of pyridinium chlorochromate (PCC) and polyaniline salts for the synthesis of isatin and its derivatives through the oxidation of indoles at room temperature or reflux in dichloromethane. In this methodology, the highest yield (88%) was obtained when indole was subjected to oxidation in the presence of PCC and polyaniline salt under 1,2-dichloroethane at 80 °C. The authors claimed polyaniline was used as a catalyst for oxidation the first time (Scheme 49).¹²⁸

The synthesis of quinoxaline derivatives in water using a polyaniline-sulfate salt catalyst and sodium laurylsulfate was

Scheme 48. Sulfoxidation Reactions by Ammonium Vanadate-Doped Polyaniline

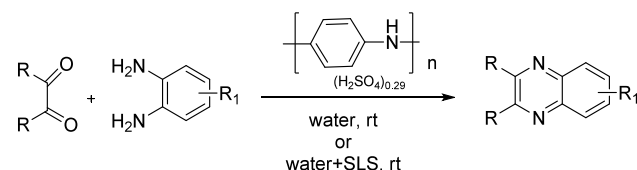


Scheme 49. Oxidation of Indoles by Polyaniline Salts



reported by Srinivas et al. (Scheme 50).¹²⁹ This methodology revealed the excellent yields of the product (70–95%) with low

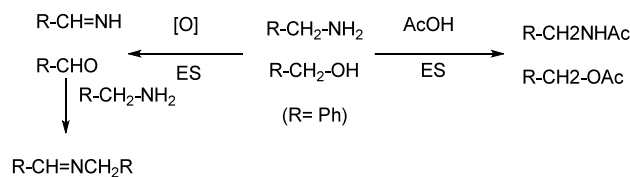
Scheme 50. Synthesis of Quinoxaline Derivatives Using a Polyaniline Sulfate Salt Catalyst



loading of the catalyst (10.5 mg, 5 wt % w.r.t. 1,2-dicarbonyl) within a short period of time (10–120 min) and has reusability.

In the year 2009, Lee et al. reported a synthesized nanoporous emeraldine salt and used it as the catalyst for the acylation/oxidation of primary amines and alcohols (Scheme 51).¹³⁰ They

Scheme 51. Acylation/Oxidation of Alcohols and Alkenes by Nanoporous Emeraldine Salts

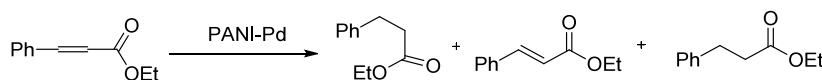


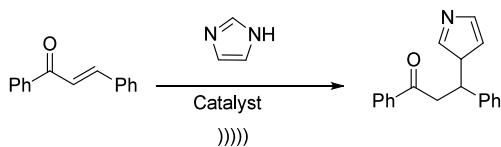
used acetic acid as an acylating agent, which provided 27–87% yields of acylated products under different solvent conditions. On the other side, in the oxidation process, the product yield obtained was 51–81%.

Patel et al. reported a polyaniline-anchored metal salt catalyst used as a Lewis acid to promote the Michael reaction of α,β -unsaturated ketones (Scheme 52).¹³¹ The reaction is performed efficiently with imidazole, acetylacetone, and ethyl acetate as Michael donors and chalcones as the acceptors under ultrasound irradiation in 2,2-dichloroethane as the solvent, which provides an excellent yield within 2 h.

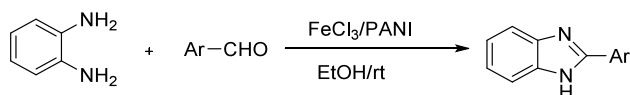
Abdollahi-Alibeik and group synthesized doped FeCl₃ with polyaniline nanoparticles and used this catalyst as a reusable and

Scheme 47. Hydrogenation of Alkynes and Cinnamaldehyde by PANI-Pd

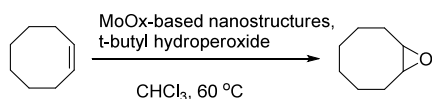


Scheme 52. Michael Reaction Catalyzed by PANI-Metal Salts

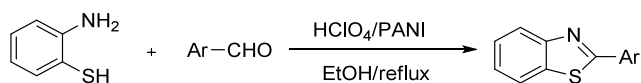
heterogeneous catalyst for the synthesis of 2-substituted benzimidazoles by the reaction of aldehydes with *o*-phenylenediamine at room temperature in ethanol (Scheme 53).¹³² The methodology provides good to excellent yield of the products (63–86%). They claimed that this reaction procedure can be complementary to existing methods.

Scheme 53. Synthesis of 2-Substituted Benzimidazoles

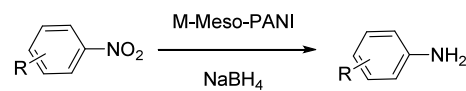
Gao et al. reported novel Fe–MoOx/polyaniline nanorods that were fabricated via in situ polymerization of Mo₃O₁₀(C₆H₅NH₃)₂₂H₂O nanowires, in which interface reactions remarkably influenced the morphology of the products and the nanorods showed high performance in cyclooctene epoxidation due to the organic–inorganic hybrid structure and Fe³⁺ additive (Scheme 54).¹³³ The activity and selectivity of the cyclooctene epoxidation over the Fe–MoOx/polyaniline nanorod catalyst (14.5 wt %) undergoes 98.8% product conversion and 97.2% selectivity.

Scheme 54. Cyclooctene Epoxidation by Fe–MoOx/ Polyaniline Nanorods

Abdollahi-Alibeik et al. developed a polyaniline-based catalyst using perchloric acid as the dopant and explored its catalytic activity for the synthesis of 2-substituted benzothiazoles through the condensation of *o*-aminothiophenol with aldehydes in good yields. This catalyst is cheap and can be reusable (Scheme 55).¹³⁴

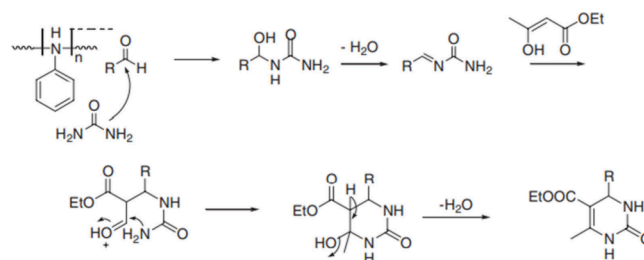
Scheme 55. Synthesis of 2-Substituted Benzothiazoles by HClO₄/PANI

Transition metal nanoparticles supported on mesoporous polyaniline (Meso-PANI) were synthesized by the self-assembly of dual surfactants followed by the in situ reduction of metal precursors in aqueous solution. Catalysts were investigated in the reduction of nitroaromatics in the presence of NaBH₄ as a reducing agent. Among the catalysts investigated, Cu (10%) *meso*-PANI exhibited the highest activity (Scheme 56).¹³⁵ Cu supported on *meso*-PANI exhibited significantly high activity compared to Cu supported on conventional PANI. Recycling

Scheme 56. M-Meso-PANI-Catalyzed Reduction of Nitroaromatics

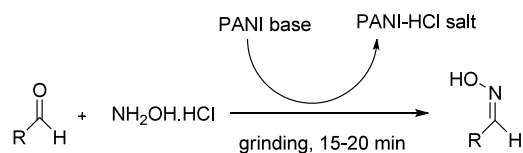
experiments suggest that the catalysts can be reused without a significant loss in catalytic activity.

A 3,4-dihydropyrimidin-2-(1*H*)-one derivative was prepared by Chabukwar et al. from aldehydes, β -ketoesters, and urea in a reaction catalyzed by using polyaniline nanoparticles under solvent-free condition reported (Scheme 57).¹³⁶ The reaction

Scheme 57. Synthesis of 3,4-Dihydropyrimidin-2-(1*H*)-one Derivative by Polyaniline Nanoparticles

carried out by sonication using 2 mg of catalyst at 45 °C optimal temperature within 40 min results in better yields (90%). This method provides advantages such as low loading of catalyst, high purity of products, high yields, and short reaction times, and the catalyst can be reusable.

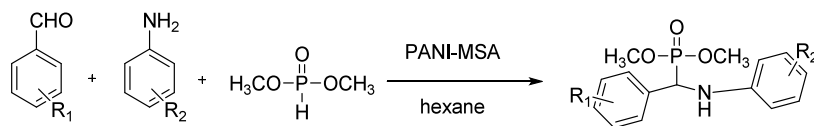
Boddula et al. developed a facile, clean, economical, efficient, and green process for the preparation of *Z*-aldoximes at room temperature under solvent-free conditions using the emeraldine base form of polyaniline as a novel catalyst (Scheme 58).¹³⁷ In

Scheme 58. Synthesis of Z-Aldoximes Using a PANI-Acid Catalyst

this methodology, PANI base absorbed the byproduct of HCl (polluting chemical) from hydroxylamine hydrochloride and converted it to polyaniline-hydrochloride salt (PANI-HCl salt). This PANI-HCl salt could be easily recovered and used in new attempts without any purification in many areas, such as catalyst, electrical, and electronics applications meant for conducting polymers. The authors claimed to use an emeraldine base as a catalyst in organic synthesis for the first time.

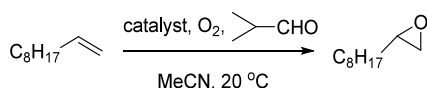
Rajender et al. developed polyaniline modified by methanesulfonic acid as a dopant. The material was coated on a glass slide/glass rod/stainless steel sheet and used as a novel reusable polymer-based solid acid catalyst in the synthesis of α -aminophosphonates with excellent yields, and the same glass slide was used for the preparation of various α -amino-phosphonates (Scheme 59).¹³⁸

Polyaniline was doped with various cobalt compounds such as cobalt(II) chloride, cobalt(II) acetate, and cobalt(II) salen and established via characterization by Kowalski et al. in 2014.¹³⁹

Scheme 59. Synthesis of α -Aminophosphonates Using a Polyaniline-Supported Catalyst

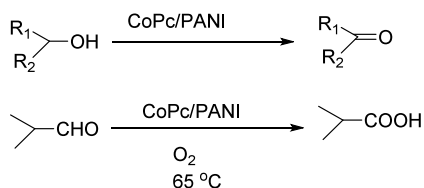
The authors studied the catalytic activity of polyaniline cobalt(II)-supported catalysts for the epoxidation of dec-1-ene with molecular oxygen at room temperature (Scheme 60). Some steric hindrance was observed when large molecules were used as doping agents, and the epoxidation of dec-1-ene occurred with excellent yields.

Scheme 60. Polyaniline-Doped Cobalt-Catalyzed Epoxidation of Dec-1-ene



Panwar et al. reported organic an inorganic hybrid catalyst synthesized by doping cobalt phthalocyanine (CoPc) on a polyaniline support (CoPc/PANI), and the synthesized catalyst exhibited higher activity for the oxidation of various alcohols to the corresponding carbonyl compounds in high to excellent yield using molecular oxygen as an oxidant and isobutyraldehyde as a sacrificial agent (Scheme 61).¹⁴⁰ Notably, the synthesized

Scheme 61. Synthesis of Carbonyl Compounds via Oxidation of Alcohols by CoPc/PANI



catalyst was found to be truly heterogeneous in nature and could be easily recovered and recycled for several recycling runs without a loss of catalytic activity.

A one-pot procedure for the synthesis of 1,4-disubstituted-1H-1,2,3-triazole derivatives via the three-component coupling reaction between terminal alkynes, benzyl halides/ \pm -halo ketones, and sodium azide in the presence of CuI nanoparticles supported on a polyaniline (Nano CuI/PANI) catalyst in water has been developed by Saadat et al. (Scheme 62).¹⁴¹ This heterogeneous catalyst showed high catalytic activity and 1,4-regioselectivity for click cyclization in water as a “green” solvent, and good to excellent yields were obtained in all cases over five repeated runs.

Krishnan and group developed modified polyaniline using ammonia as a dopant and graphitic carbon nitride for the composite (ammonia-doped polyaniline–graphitic carbon nitride nanocomposite) and used it as a heterogeneous green

catalyst for the synthesis of indole-substituted 4H-chromenes (Scheme 63).¹⁴² This methodology provides reusability and a low environmental factor (0.13) and imparts very high atom economy (94%).

Siwal and group reported polymer-supported palladium nanoparticles using potassium tetrachloropalladate as the precursor of palladium nanoparticles.¹⁴³ The polymer-supported palladium nanoparticles were successfully used as an electrocatalyst for the methanol oxidation reaction in alkaline media.

Chen and group developed Pd–Au bimetallic catalysts that were supported on polyaniline-functionalized carbon nanotubes (Pd–Au/PANI-CNT) and used them as catalysts for the N-formylation of amines with CO₂ and H₂ (Scheme 64).¹⁴⁴ This methodology provides excellent yield of the product (98.3%) for the N-formylation of pyrrolidine.

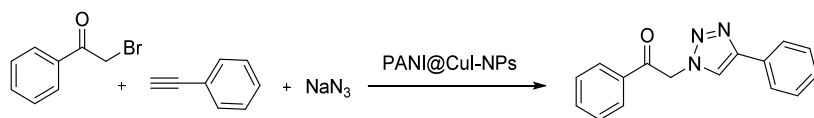
Mahato et al. developed an iron–polyaniline composite nanofiber via the in situ polymerization of aniline monomers followed by reductive deposition of Fe(0) on a PANI matrix. Fe0-PANI was used as a catalyst in a chemoselective one-pot strategy for the deprotection of oxime (Scheme 65).¹⁴⁵ This methodology showed excellent chemoselectivity (>99%), and the catalyst could be reused 10 consecutive times.

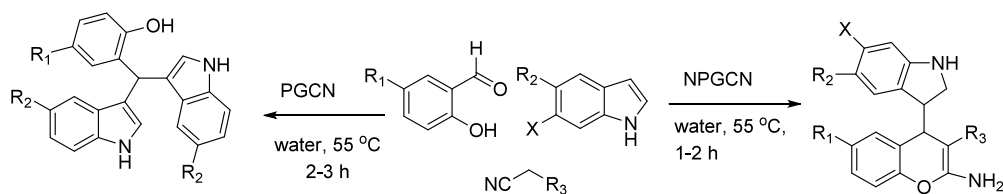
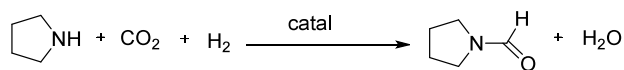
Patel et al. prepared a polyaniline-supported FeCl₃ catalyst that was used as a heterogeneous catalyst in the Biginelli reaction for the synthesis of dihydropyrimidinones from aldehydes, 1,3-diketone, and urea with excellent yields of the products (65–90%) (Scheme 66).¹⁴⁶ The solvent study indicated acetonitrile (ACN) is best solvent for this reaction, which gives greater yield. The group revealed that the reaction was selective for aromatic aldehydes.

Wang and his group reported the synthesis of α -chloro aryl ketones in the presence of visible light by using a PANI (polyaniline)-g-C₃N₄-TiO₂ composite catalyst in methanol (Scheme 67).¹⁴⁷ Excellent yields were achieved for the products; of the *para*-substituted aryl diazonium salts, the cyano group-containing one provided the highest yield (78%), but the yield of 4-chlorophenyl diazonium tetrafluoroborate was comparatively lower (60%). The catalyst can be reused 8 consecutive times.

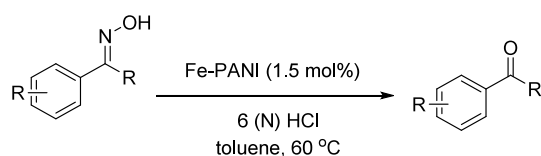
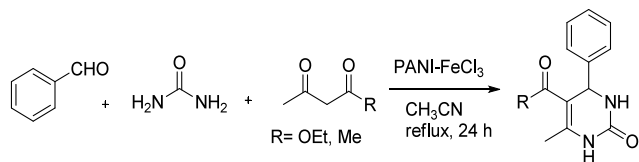
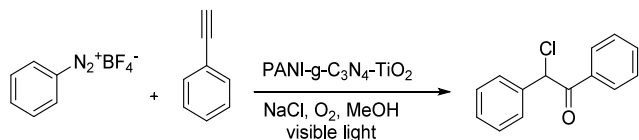
PANI was successfully synthesized by a simple sonochemical method. The uniform Fe nanoparticles were dispersed on polyaniline and used for the direct conversion of synthesis gas into lower olefins by Gu et al. (Scheme 68).¹⁴⁸ They compared the catalyst to active carbon and N-doped active carbon, and polyaniline as a support for Fe catalysts showed higher selectivity for lower olefins (C₂–C₄=). The C₂–C₄= selectivity reached ~50% at a CO conversion of 79% over a 10 wt % Fe/polyaniline catalyst without any promoters.

Scheme 62. PANI@CuI-NPs-Catalyzed Synthesis of 1,4-Disubstituted-1H-1,2,3-triazole Derivatives



Scheme 63. Synthesis of Indole-Substituted 4*H*-Chromenes Using a Modified Polyaniline CompositeScheme 64. Pd-Au/PANI-CNT-Catalyzed *N*-Formylation of Pyrrolidine

Scheme 65. Chemoselective Deprotection of Oxime Using an Iron-Polyaniline Nanofiber

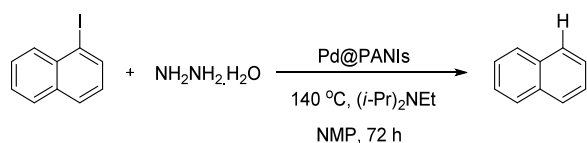
Scheme 66. Bigineli Reaction Catalyzed by a Polyaniline-Supported FeCl₃ CatalystScheme 67. Synthesis of α -Chloro Aryl Ketones Using Polyaniline-g-C₃N₄-TiO

Scheme 68. Synthesis of Lower Olefins Using Polyaniline Fe Nanoparticles



Liu and group developed a series of polyaniline-supported palladium nanoparticles by using electron-rich and electron-deficient substituted aniline with palladium chlorides (Scheme 69).¹⁴⁹ The group studied the Ullmann reaction of aryl iodides for the generation of biaryls. Mechanistic studies revealed this is due to the stronger coordination of the nitrogen ligands on the

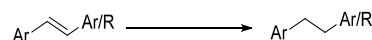
Scheme 69. Ullmann Reaction Catalyzed by Polyaniline-Supported Palladium Nanoparticles



electron-enriched PANI support with the Pd centers, higher adsorption rates of the reactant on the electron-enriched Pd@PANI catalysts, especially those promoted by the Pd loading, and the easier generation and higher ratio of the Pd(0) species in the catalyst, which are the active catalysts in the Ullmann reaction responsible for the product yields and the TONs of the reactions.

Patel et al. reported a celite polyaniline-supported palladium catalyst for chemoselective hydrogenation reactions (Scheme 70).¹⁵⁰ The mild reaction conditions allow the control over the

Scheme 70. Chemoselective Hydrogenation Reactions Using a Polyaniline Palladium Catalyst



reactions and excellent selectivity is achieved in number of conversions. Hydrogenation of a carbon=carbon double bond was favored over other polar π -bond systems, while labile functional groups such as benzyl ether, benzyl esters, cyano, nitro, and halogen remained unaffected. Primary amines were converted to *N,N*-dimethyl amines with formaldehyde, and the double bond of coumarin was selectively hydrogenated without opening of the lactone functionality.

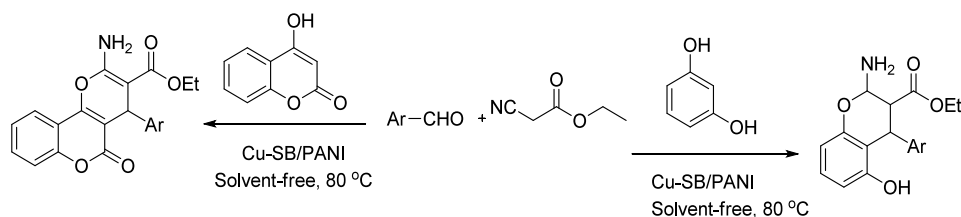
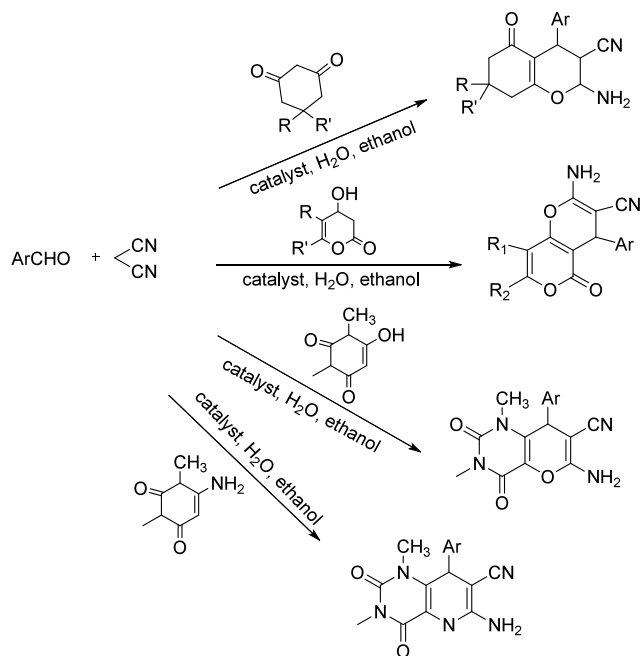
Siddiqui et al. developed a copper Schiff base-functionalized polyaniline (Cu-SB/PANI) and explored its catalytic activity for the synthesis of 2-amino chromene derivatives.¹⁵¹ (Scheme 71) The catalyst provides excellent yields of the product (95–97%) within short periods of time (6–8 min). The catalyst can be reused several times without any loss of catalytic activity.

Fathabadi et al. reported that polyaniline, polyaniline/SiO₂, and poly(4-vinylpyridine) are highly effective base catalysts for the synthesis of tetrahydrobenzo[*b*]pyran and 3,4-dihydropyran[*c*]chromene derivatives via the one-pot three-component condensation reaction of aryl aldehydes, malononitrile, and α -hydroxy- or α -amino-activated C–H acids such as 1,3-cyclohexanedione, dimedone, 4-hydroxy-6-methylpyrone, 4-hydroxycoumarin, 1,3-dimethylbarbituric acid, and 1,3-dimethyl-6-amino uracil.¹⁵² (Scheme 72)

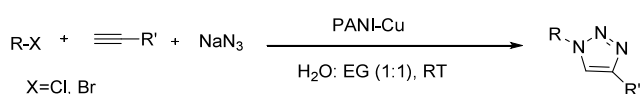
The reduction of nitrophenol was efficiently catalyzed by graphene-TiO₂-polyaniline nanocomposite as reported by Thakare et al.¹⁵³ Without the need for NaBH₄, the low-cost GPTiO₂-PANI photocatalyst demonstrated the chemoselective reduction of a variety of nitro substrates into the corresponding amines with reduced functional groups. The authors also claimed that the current method is an alternative for noble metals and NaBH₄. The photocatalytic system GP-TiO₂-PANI can be readily and affordably assembled. Additionally, the catalytic reaction can be repeated up to five times without losing its activity.

Chetia's group reported a click reaction that was catalyzed by a copper-containing polyaniline nanocomposite (Scheme 73).¹⁵⁴ In this methodology, the reaction mixture was maintained at room temperature in the presence of 10 mol %

Scheme 71. Synthesis of 2-Amino Chromene Derivatives Using Cu-SB/PANI

Scheme 72. Synthesis of Tetrahydrobenzo[*b*]pyran and 3,4-Dihydropyrano[*c*]chromene Derivatives Using a Polyaniline/SiO₂ Catalyst

Scheme 73. Click Reaction Catalyzed by a Polyaniline Copper Nanocomposite



catalyst in different solvent conditions, affording good to excellent yield of products. When H₂O–ethylene glycol (1:1)

with ascorbic acid is used as the solvent, it gives the highest yield (96%). Hence, the authors claimed this catalyst is an efficient heterogeneous catalyst for the synthesis of 1,4-disubstituted-1H-1,2,3-triazoles.

3. MECHANISM FOR POLYANILINE-SUPPORTED CATALYZED ORGANIC TRANSFORMATIONS

A representative mechanism for the synthesis of the β -aminocarbonyl compound via a Mannich reaction was described (Figure 8). In the mechanism for the synthesis of the β -aminocarbonyl compound, the aluminum center of NDPANI coordinates with the carbonyl group of aldehyde, acts as an activating agent to make an electrophilic center, and supports the nucleophilic attack of the free amine to form an aldimine. Then, the enol form of the ketone reacts with aldimine to form a β -aminocarbonyl compound.⁸⁰

4. COMPARISON OF CATALYSTS

The comparison of polyaniline-supported catalysts with other reported catalysts for the synthesis of β -aminocarbonyl compounds is of great importance. After a well-documented comparison, it was observed that polyaniline-supported catalysts are better catalysts than other catalysts in terms of percentage yields, short reaction time, and solvent-free reaction conditions, which makes a greener protocol for the synthesis of β -amino carbonyl compounds (Table 2).

5. FUTURE SCOPE OF POLYANILINE-SUPPORTED CATALYSTS IN ORGANIC SYNTHESIS

Due to the advantageous nature of polyaniline, it is widely used as a catalyst for many organic transformations under green reaction conditions. The core applications in organic transformations have yet to be explored with the modification of polyaniline using many dopants such as nontoxic dopants for the green synthesis of organic compounds and chiral auxiliaries,

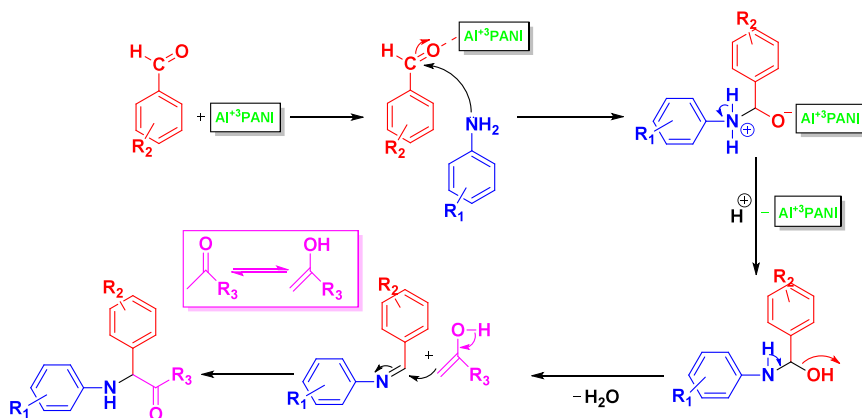


Figure 8. Representative mechanism of a Mannich reaction catalyzed by alum-doped nanopolyaniline.

Table 2. Comparison of Polyaniline-Supported Catalysts with Other Reported Catalysts for the Synthesis of β -Amino Carbonyl Compounds

catalysts	reaction conditions	yield (%)	ref
calix[4]arene	acetophenone, NaOH in water, rt, 24 h, 2 mol % catalyst	77	155
PS-SO ₃ H	acetophenone, water, 30 °C, 24 h, 1 mol % catalyst	75	156
H ₃ PW ₁₂ O ₄₀	acetophenone, water, rt, 18 h, 0.02 g of catalyst	76	157
ZrOCl ₂ ·8H ₂ O	cyclohexanol, solvent-free, rt, 0.5 h, 0.05 g of catalyst (15 mol %)	75	158
Troger's base derivatives	acetophenone, water, rt, 9 h, 0.06 mol % catalyst	80	159
NDPANI	acetophenone, solvent-free, rt, 7 h, 0.116 g of catalyst (3 mol %)	93	80
PANI-AgNO ₃ -PTSA	cyclohexanol, water, rt, 1.1 h	96	78
PANI-FeCl ₃	cyclohexanone (2.6 g, 26.0 mmol), rt, 6 h, 0.14 g of catalyst	72	75
PANI/SiO ₂	acetophenone (5 mmol), catalyst (0.1 g), ethanol	85	13
PANI-HBF ₄	cyclohexanone (2.6 g, 26.0 mmol), rt, 6 h, 0.14 g of catalyst, solvent-free	86	72
PANI-PTSA	cyclohexanone (2.6 g, 26.0 mmol), rt, 6 h, 0.14 g of catalyst, solvent-free	85	72
PANI-HBF ₄ -DHS	cyclohexanone, solvent-free, rt, 6 h, 25 wt % catalyst	80	14

making it a suitable catalyst for asymmetric synthesis and other applications in the future. Asymmetric synthesis has high-demand applications in pharmaceuticals and natural product synthesis. Our group started work on chiral auxiliary-modified polyaniline for asymmetric organic synthesis, and in the near future it will give fruitful results.

6. CONCLUSION

In summary, polyaniline is a highly demanding conducting polymer among all polymers, and modified polyaniline-supported catalysts successfully catalyzed many important organic reactions and provided many advantages, such as nontoxic and environmentally stable catalysts, most reactions are under net reaction conditions, high yields, and low cost; additionally, the catalyst can be easily recovered and reused several times without hampering the catalytic activity. Hence, polyaniline can be a promising catalyst for future organic transformations under green reaction conditions.

AUTHOR INFORMATION

Corresponding Author

Satyaranjan Behera – Department of Chemistry, Utkal University, Bhubaneswar 751004, India; orcid.org/0000-0002-7610-1989; Email: behera.satyaranjan4@gmail.com

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.4c04352>

Notes

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