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Nobel Metal Decorated TiO$_2$ Catalyst Coated On Cordierite Monolith for High Turnover Frequencies in Carbon-Nitrogen Coupling Reactions

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ABSTRACT: - A Pd-doped TiO$_2$ catalyst was used to control the reaction of many aryl-amines with an aryl halide with an amine. Catalyst Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ is effective in the C-N coupling reaction and can be re-used at least five times in this reaction without a major reduction in its Pd-doped catalyst; a series of stepwise sequences of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ have been coated for cordierite monolith. The coating on cordierite, as observed from the XRD analysis, is nano-crystalline. The C-N bonding crystalline catalyst was used to synthesize aryl halides and amines. C-N products have been synthesized using spectroscopy with ^{1}H NMR, ^{13}C NMR, and FTIR. This diagram shows a strong selectivity in the coupling to C-N. Turn-over Frequency (TOF) was observed twice for each high-dose reaction.

Keywords: - Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$, Buchwald-Hartwig, Amination, Recycling.

I.   INTRODUCTION

In the past 30 years, there has been a gradual increase in the use of monoliths as catalyst supports. During this period, monoliths have mostly been used in environmental applications [1]. Some of the applications in which these benefits have proven useful include exhaust gas treatment [2-3]. Monolithic catalyst supports can be an attractive replacement for conventional carriers in heterogeneous catalysts. Monolithic structures, either metal or ceramic, consist of single blocks of small (0.5-4 mm) parallel channels with a catalytic wall. In the application of a monolithic catalyst, one should first determine what the requirements for the support are. The most common material for monolithic structures is cordierite and as ceramic material which consisting of magnesia, silica, and alumina in the ratio of 2:5:2), because this material is very well suited for the requirements of the automotive industry. The main reasons for this are that it has a high mechanical strength, high temperatures, temperature shocks, and has a low thermal expansion coefficient [4-6]. Cordierite fuel cells have been used in various ways, such as brake support, catalytic converter, hot gas, and air pressure, as well as have been removed from the water source. The cordierite monolith was designed for the application of their optical properties to produce a high volume of gas in contact with active additives, high geometry, low pressure, high operating power, short diffusivity, high thermal stability, low humidity, the expansion assemblies and water resistance [7-8].

There is a level of cordierite monolith needed to cover the layer of concrete, which increases the surface area and is used to connect with chemicals. This is known to be supported by a coating system [9-10]. Pd^{+2} ion covers the surface of solid material, and it might be possible to stabilize the actives of Pd type and cure faults. Pd doped nano particles are used in catalysis and are not only important for function [11-12] but also scientifically known for the relationship between catalytic behavior, particle size, and diffusion patterns, and information was surrounding [13-14]. Pd^{+2} catalyzed cross-coupling reactions have provided as a prevailing means for proficient carbon–carbon and carbon–heteroatom bond formations in the synthesis of pharmaceuticals, fine chemicals and advanced materials over the past decades [15-18]. The carbon-nitrogen coupling reaction has been extensively used in synthetic routes for pharmaceuticals and natural products [19]. However, little interest has been paid to its applications and advancement of polymer chemistry [20-22].

From literature, Nijhuis et al. [23], studied conversion of doped monolith catalysts and revealed a suitable pump. Boger et al. [24] have been considered for the high-efficiency human catalytic activity and the usefulness of aromatic hydrocarbons in the chemical industry, Beau seigneur et al. employed for different systems in the colloidal coating method [25]. The Silica coated on monolith from the sol-gel coating method has been developed by Zwinkels et al [26]. A detailed alumina slurry coating on monolith has been discussed by Blachou et al. [27].

Buchwald and Hartwig individually proposed the procedures for the palladium-mediated amination of aryl halides [28-29]. The Buchwald-Hartwig reaction represents a transition metal-promoted versatile catalytic method for the formation of C-N bonds to obtained substituted aryl amines [30-31]. Heterogeneous catalysts has achieved precedence over homogeneous catalysts because of their easy handling, effortless isolation, and reusability [32-33]. To increase the efficiency and stability of homogeneous catalysts, several approaches have been proposed following immobilization on different heterogeneous supports [34-36]. A number of Pd/heterogeneous supported catalysts have been reported for the Buchwald-Hartwig reaction by several research groups [37-40].

Several conditions of reaction have been higher for Buchwald–Hartwig amination reaction; it is used as a beneficial and synthetically significant way f or synthesizing aryl and hetero aryl amines. Compare with a different approach to C-N generation [41]. The Pd reactive reactants in the reaction do no longer include tremendously in reactive materials [42]; it may be lead to safety problems. Pd catalyzed N-arylation reactions have been done in several attempts to locate appropriate catalyst systems under different conditions due to the importance of the recovery of the Pd metal. The synthesis of arylamines generally relies on C-N coupling between amines and aryl halides using catalysts based on transition metals like palladium,[43] copper,[44] nickel,[45] iron,[46] cobalt,[47] and rhodium. Palladium-mediate cross-linking of aryl halides in N-H contains a compound called the Buchwald's-Hartwig amination reactions that is proposed to be a good mediator for C-N synthesis and its management and biological control for total arylamines [48]. In particular, palladium-catalyzed arylamination became important and widely used for the production of the C-N bond [49].The Buchwald-Hartwig coupling reactions have been considered in different kinds of heterogeneous Pd substituted catalyst systems [50-56]. The preparation of aromatic amines in the general method has emerged as an extremely in the bond formation of the Pd-catalyzed C-N coupling reaction [57-59]. Heterogeneous Pd catalysts used as an extraordinarily useful strategy in organic synthesis have emerged in the synthetic area through the Pd-catalyzed organic reactions [60-62].

In the previous study shows that the Pd doped Titania catalyst for C-N coupling reaction with different solvents, bases and oxidants were not yet been reported. Therefore, the present study revealed C-N coupling reaction with 3% Pd^{+2} doped Titania ($Ti_{0.97}Pd_{0.03}O_{1.97}$) using glycine as fuel by solution combustion method. The prepared catalyst was coated on cordierite monolith by simple solution combustion method. We studied C-N coupling reaction (Buchwald and Hartwig) with effects of aryl halides and amines using different solvents, bases and oxidants using toluene as solvent with different reaction conditions.
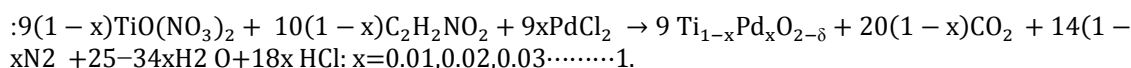
II.   EXPERIMENTAL

2.1 Materials

Cordierite ceramic honeycomb, γ-Al_2O_3, Titanium tetra isopropoxide (Ti $(OC_3H_7)_4$), Titanyl nitrate (TiO (NO_3), Palladium chloride ($PdCl_2$) and Glycine (NH_2CH_2COOH) were purchase from Merck. Aryl halides (Iodobenzene and Bromobenzene) and amines (aniline) were used as purchased without further purification and TLC plates.

2.2 Synthesis of $Ti_{0.97}Pd_{0.03}O_{1.97}$ Powder Catalyst

The solution combustion method for synthesized $Ti_{0.97}Pd_{0.03}O_{1.97}$ has been used in this study. A 300 mL crystallizing dish included TiO $(NO_3)_2$ (9.89 mmol), made of titanium tetra isopropoxide, $PdCl_2$ (0.31 mmol) and NH_2CH_2COOH (10.99 mmol). The combustion of the starting materials accompanied by dehydration was controlled during a silted furnace preheated to 350 ^{o}C. The blend was kept inside the furnace, every 20 minutes for all the carbon content to burn up. Then the dish was removed from the oven, and the powder could be cooled and extracted from the catalyst. During a pestle and mortar, the catalyst was ground and marked by powdered XRD. The reaction to combustion was given via equation (1).

$:9(1 − x)TiO(NO_3)_2 + 10(1 − x)C_2H_2NO_2 + 9xPdCl_2 → 9 Ti_{1−x}Pd_xO_{2−\delta} + 20(1 − x)CO_2 + 14(1 −$
$xN2 +25−34xH2 O+18x HCl: x=0.01,0.02,0.03⋯⋯⋯1.$

2.3 Procedure for Alumina (γ-Al_2O_3) coated honeycomb monolith

Before coating on the monolith, γ-Al_2O_3 is insulation and monoliths to enhance the surface area, and it is held on to TiO_2. A warm furnace required 16 mmol Al $(NO_3)_2$ and 9 mmol of Glycine to react to the reaction. The model was made, a thin film applied to the flask and put in a burner, and the monolith was removed from the

furnace after 15 minutes and cooled down. The process remains unchanged until the thickness of the coating γ-Al_2O_3 is increased up to 2 to 2.5% of the weight of the cordierite monoliths.

2.4 Growing γ-aluminates on cordierite honeycomb by solutions of combustion methods.

Take 1.4 cm thick, 2.6 cm long cordierite-coated monolith with 200 cell / inch^2 γ-Al_2O_3 was coated with Al $(NO_3)_2$ and Glycine (NH_2CH_2COOH) aluminum nitrate water-soluble cordierite. The dry ceramic monolith is fired at 400 ^{0}C and dipped into the solution. Repeated drying processes cause to be the coating reactions and chemicals in ceramic fuel below in equation. (2)

$$2\,Al(NO_3) + 3NH_2CH_2COOH \xrightarrow[400°C]{} \gamma - Al_2O_3 + 6CO_2 + 9N_2 + 9H_2O \cdots\cdots\cdots (2).$$
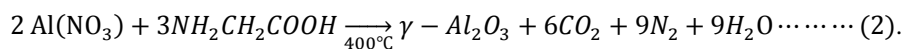
2.5 Coating of $Ti_{0.97}Pd_{0.03}O_{1.97}$ nanocatalyst over Alumina coated cordierite monolith

The theoretical use of Ti (OC_3H_7), $PdCl_2$, and $C_2H_5NO_2$ are for $Ti_{0.97}Pd_{0.03}O_{1.97}$. The coating of three catalysts, Pd doped TiO_2 ($Ti_{0.97}Pd_{0.03}O_{1.97}$), TiO_2, 9,7mmol $(NO_3)_2$, $PdCl_2$, 0.3 mmol, and Glycine 11mmol, dissolved in water to form a solution is a tough process. γ-Al_2O_3 coated honeycomb is dipped in the reaction and quickly heated at 400 ^{0}C, respectively. For honeycomb weight, dip-dry-firing was carried out up to 2-3% of the catalytic weight. The volume of the catalyst prepared on the monolith of cordierite is around 110 mg; Figure 1 shows the total weight of the sample of the cordierite monolith. The surface reaction of the monolithic ceramic γ-Al_2O_3 is often stated in the following equation (3).

$$9(1-x)TiO(NO_3)_2 + 10(1-x)C_2H_2NO_2 + 9xPdCl_2$$
$$\rightarrow 9\,Ti_{1-x}Pd_xO_{2-\delta} + 20(1-x)CO_2 + 14(1-x)N_2 + (25-34x)H_2O + 18x\,HCl: x$$
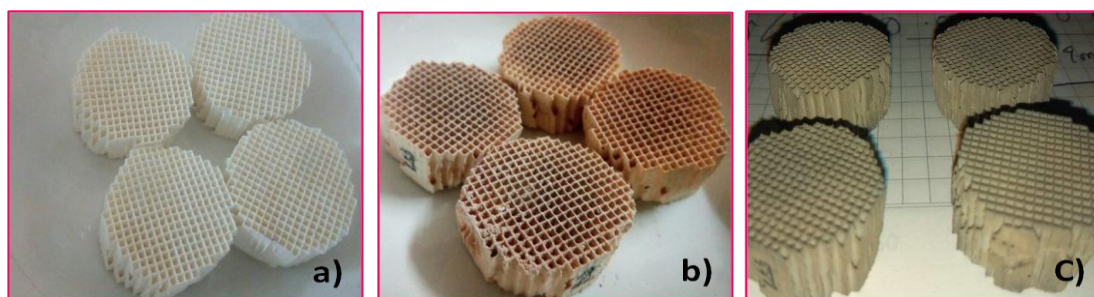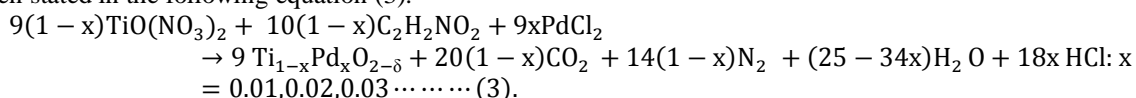$$= 0.01, 0.02, 0.03 \cdots\cdots\cdots (3).$$

Figure.1. Photographs of (a) alumina-coated honeycomb monolith, (b) top view and side view of the catalyst-coated monolith, or (c) catalyst-coated honeycomb after several reaction cycles.

The $Ti_{0.97}Pd_{0.03}O_{1.97}$, the propellant supporter, was designed as described in the experimental part and then used in the experiment. The parameters of the system are evaluated by conserving the capacitors. The effects of the palladium doped TiO_2 catalyst were demonstrated in the formation of anionic catalyst products, as shown in Table.1. The $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst showed high activity in selectivity and bonding. Pd-catalyzed C-N is synthesized as a common method for the preparation of aromatic amine. [63-65].

Table.1: Coating of Al_2O_3 and $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst on honeycomb.

Sl No	Honeycomb (g)	Honeycomb+ Al_2O_3 (g)	Honeycomb + $Ti_{0.97}Pd_{0.03}O_{1.97}$ (g)	Pd doped TiO_2 in Honeycomb (mg)
1	2.5327	2.8090	2.9052	**97.2**
2	2.5954	2.8449	2.7326	**182.9**
3	2.5703	2.3529	2.7326	**161.3**
4	**2.5562**	**2.6126**	**2.8196**	262.4

2.6 General Experimental procedure for Buchwald-Hartwig Couple reactions

The solution contains aryl halide (2.5 mmol), amine (0.6 mmol), K_2CO_3 (3.0 mmol), and Pd doped TiO_2 catalyst (0.03%) using toluene (10 mL). The mixture was incubated at a temperature of 110 $°$ C and reached 08−18 h. TLC was used to check the final product of the reaction. First, the solvent is used to remove the solvent and purify it with $MgSO_4$, which is then purified. This good product is always produced after antibiotics. The Chromatography was used for further measurements, and all of these products are measured in GC. The reaction mixture was heated to 110 °C for 12 hours as iodobenzene (2 mol), amine (2.4 mol), dipropyl amine ($C_6H_{15}N$) (3 mol), and oxidant (0.03 mol %) and toluene (10 mL) of tert-butyl hydroperoxide (T_BH_7Ox). This mixture was heated, stirring with the Celite (silica) bed in hot conditions. The study showed a 90% effect on the GC test. Subsequently, the filtrate was used for the reaction without adding, the stoichiometric

composition, and the reaction condition allowed. After 12 hours, the GC reaction with the reaction mixture showed that there was not before the reaction. 5 ml ester is added to the reaction mixture and stirred five minutes after the reaction time. The burning machine is separated by centrifugation after this time. In other systems, the refined oils use EtOH (ethanol) and dried under a vacuum. Then, the restored pump is employed for an additional run.

Figure.2. Photograph of a) C-N coupling reaction setup b) UV cabinet c) Rota evaporator d) Celite bed

III. RESULTS AND DISCUSSION

3.1 Powder X-ray Diffractometer analysis (PXRD)

The solution combustion method TiO (NO$_3$)$_2$, PdCl$_2$, and (NH$_2$CH$_2$COOH) was formed at 350 °c temperature for catalytic tubes Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$. The TiO$_2$ crystallize damage was substituted by the Pd. Figure 3 displays XRD and Rietveld of XRD for 3% Pd and TiO$_2$ atoms. There are no different amounts of PdO or Pd iron. The angle of the grating is = 3,796 Å and c = 9,534, a = 3,796 c and a = 9.533 c Å, a = 9,533 c. Pd^{2+} is 0.64 Å close to that of Ti^{4+} (0.605 Å). The morphological data of Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ are 2.5 cm thick and overlaid with Mg$_2$Al$_4$Si$_5$O$_{18}$. We will see (101) the output of the XRD output in section 25.3∘, and therefore the difference between the closed monoliths is shown in Figure 3. Each Monolith features a clearly defined path. Therefore, the higher area is exposed to reactors. The color of the plaster is brown. The thickness of the crystals is 8 ± 2 nm calculated by the half-wavelength (101) of the solid line (Figure 3) using the Scherrer's method (d = 0.9λ / β cosθ) and therefore the powder and surface also are an equivalent size is predicted because the half-width of (101) is that the same. On a water-resistant surface, a coating of the coated monolith (HC) is applied. The entire catalytic reaction of the HC catalyst is present within the solvent. The reaction mixture was stay within the 110 °C hot water bath. The conversion speed of the catalyst is high and then separates the reaction mixture and solvent from the HC catalyst.
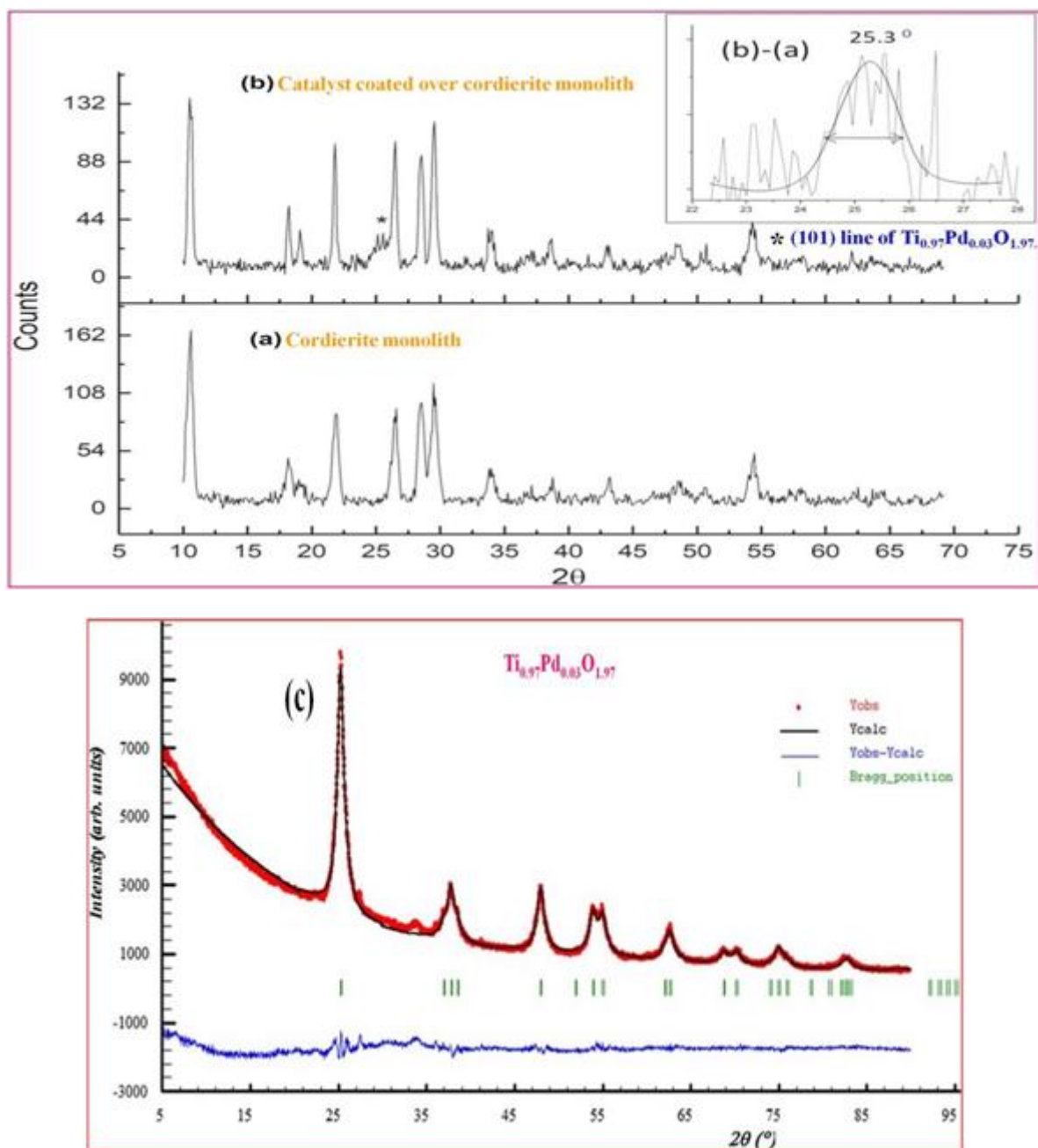
Figure.3. Powder XRD patterns of (a) cordierite monolith, (b) catalyst coated over cordierite monolith, c) Rietveld refined pattern of the Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ catalyst.

3.2 Field Emission-Scanning Electron Microscope studies (FESEM)

The SEM experiments showed that palladium doped TiO₂ did not affect the morphology and structure of TiO₂ nanoparticle. FE-SEM was employed to study the properties of the synthesized catalyst. The SEM images are also utilized to examine the approximate particle size of the catalyst. Figure.4. Shows typical SEM images of 0.03% Pd doped TiO₂ powder catalyst at a couple of magnification. The above figures reveal that the approximate particle size is between 1μm to 10μm, and however, it is observed that distinct particles can agglomerate more into larger particulates of 100 to 200 nm.
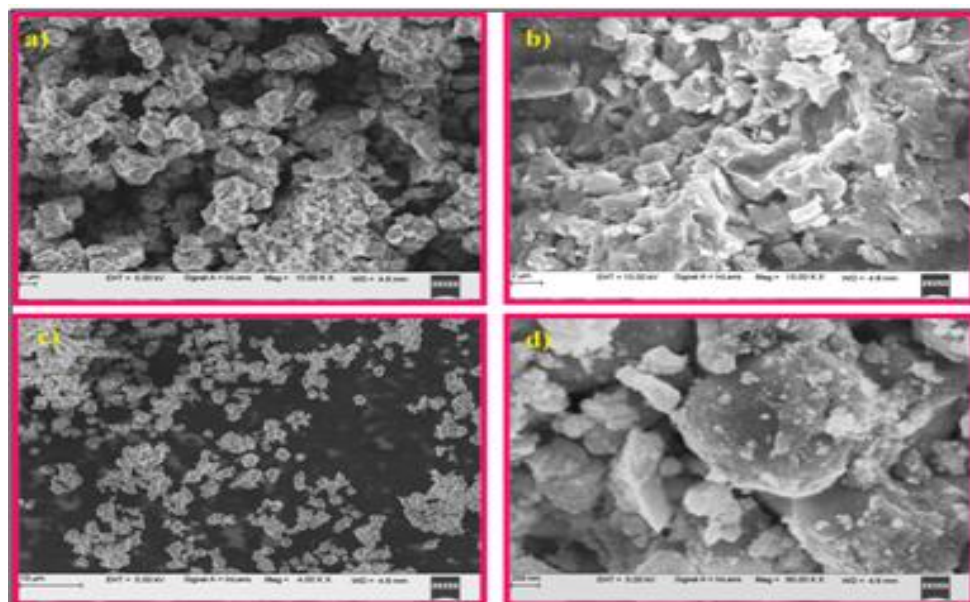
Figure.4. SEM images of a) 1µm b) 2µm c) 10µm d) 200nm sizes of 0.03% Pd doped TiO₂

3.3 Energy-dispersive X-ray spectroscopy analysis (EDAX)

The EDS spectral analysis made to randomly selected points of SEM images showed for the 0.03% of Pd doped TiO_2 titanium, palladium, oxygen, and carbon as the main elements, whereas the noble metals are not detected. The existence of Ti, Pd, C, and O has been detected. The presence of the carbon peak is because of the use of concentrated nitric acid during the preparation of Pd doped TiO_2 of catalyst. The Figure 5 shows the EDAX spectrum of sample Pd doped TiO_2 shows various atomic percentages such as titanium, palladium, oxygen, and carbon shows 18.21%, 0.79%, 54%, and 27% of carbon impurity respectively are shown in Figure.5. The analysis shows that Pd in the measure 0.79% is provided, which is similar to the preparation of the compositions. In the EDAX analysis, the existence of Pd supports the replacement of Pd ion in the TiO_2 lattice.
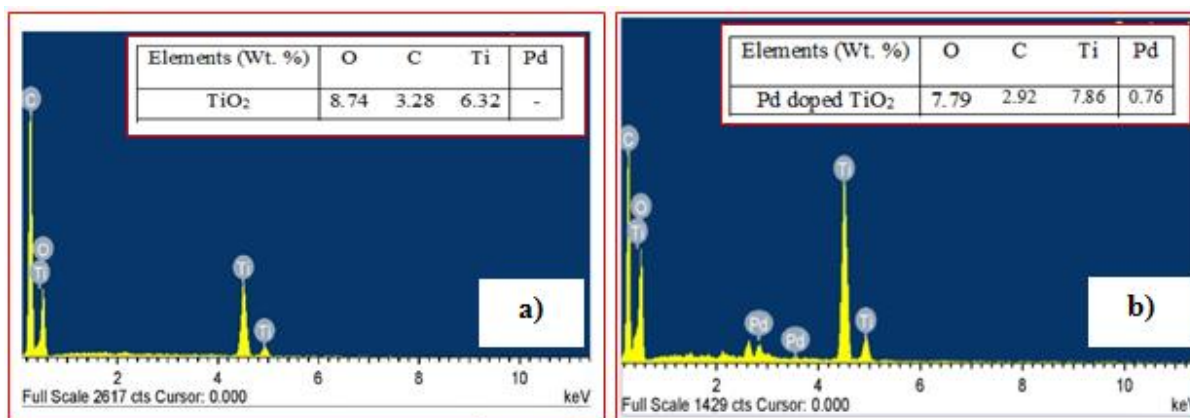
Figure.5. EDX images of 0.03% Pd doped TiO₂

3.4 X-ray photoelectron spectroscopy (XPS) studies

Before the reaction was shown in the Figure 6, the XPS of Ti (2p) on $Ti_{0.97}Pd_{0.03}O_{1.97}$ monolith was calculated. Ti is 459.2 eV and 464.9 eV respectively for the state potential +4 of Ti (2p3/2) and Ti (2p1/2). The $Ti_{0.97}Pd_{0.03}O_{1.97}$ XPS of Pd (3d) was exposed before exposure to aromatic fuel. $Ti_{0.97}Pd_{0.03}O_{1.97}$ and 337.25 eV and 341.10 eV monoliths, respectively, have a combined power of Pd (3d5/2) and Pd (3d3/2). In PdO 335.1 eV and 336.4 eV respectively, [66] the Binding Energies Pd (3d5/2) and PdO are observed. The coating state of Pd in $Ti_{0.97}Pd_{0.03}O_{1.97}$ of the monolith coating is +2, and therefore the bond strength of the Pd^{2+} ion and TiO_2 matrix is above that of PdO, and Pd^{2+} ion is ionic than that of PdO. The added strength Pd (3d) core of $Ti_{0.97}Pd_{0.03}O_{1.97}$ honeycomb coating is that the same as $Ti_{0.97}Pd_{0.03}O_{1.97}$ powder [67]. The dependence of the C 1s is 285.56 eV, 284.3 eV, and 287.1 eV, respectively. The instance shows the high number of O 1s seen in parentheses. The 2 peaks present during this figure.6. Are expressed in O 1s and OH two, respectively. Attempts to limit the utmost number of O1s at about 530.5 eV and therefore the peak at 528.5 eV are related to OH individually.
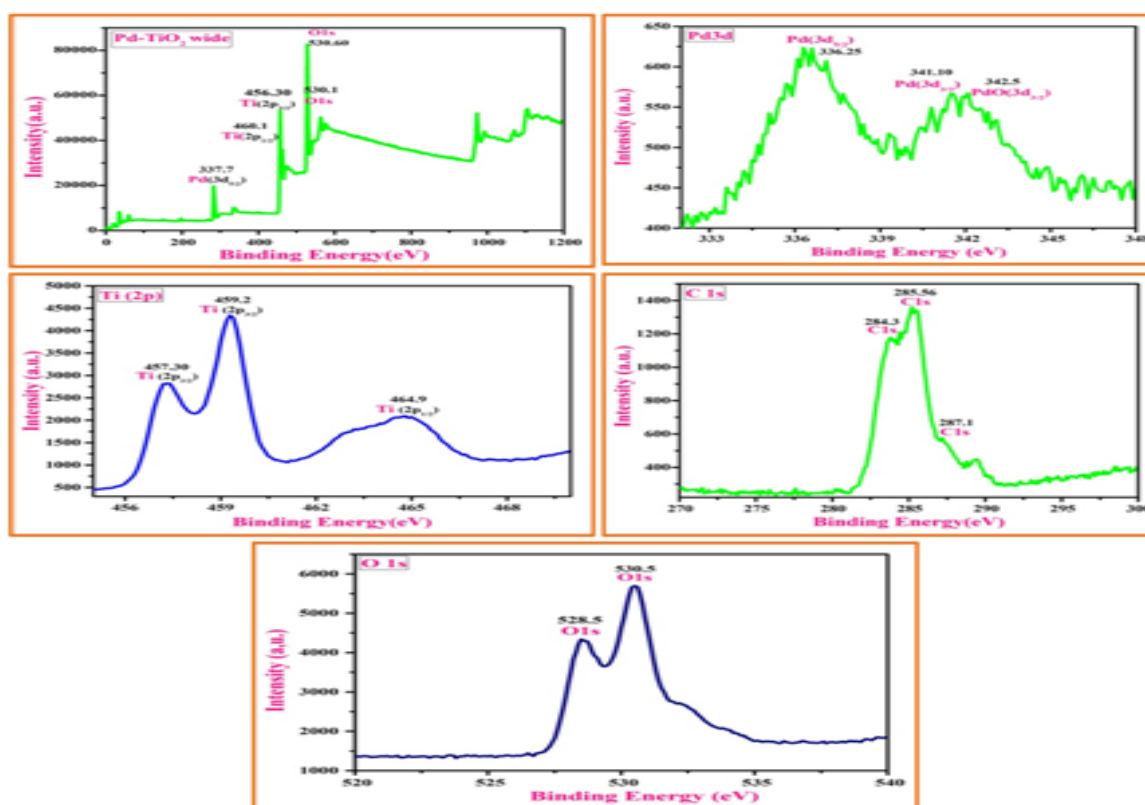
Figure.6. Core level XPS of (a) Pd doped TiO$_2$ (b) Pd (3d), (c) Ti (2p), (d) C 1s and (e) O 1s in Ti$_{0.09}$Pd$_{0.03}$O$_{1.97}$-catalyst

3.5 Fourier transforms Infrared spectroscopy (FT-IR) analysis

The free N-H absorption in secondary amine has been reported to be in the region of 3385 cm. The significant fall in the frequency observed is due to association by intermolecular H-bonding in the solid phase spectrum. The frequency change of this order might well arise from a change of state due to the possibilities of interactions of hydrogenic vibrations in neighboring molecules in the solid-state. It is not possible to do more than indicate the approximate range of 3400-3100 cm°' for associated absorptions of this type. Accordingly, we find three N-H absorptions, which are all weak at 3120, 310, and 3180 cm° in the spectrum of diphenylamine. The N-H deformation absorption is usually very weak in secondary amines as indicated in Table.2. The FT-IR spectra of Pd doped TiO$_2$ and diphenylamine are shown in Fig. 7 a). FT-IR sample from Fig. 7 b). Point to the mixture of two-dimensional structures within the vitreous matrix. The larger range appears in 3854-3751 cm^{-1} is given by the various functions of -OH and therefore the numbers 1767 and 1781 cm^{-1} are O-H stretching guns. The rat is assumed to be ~ 2341 cm^{-1} as results of the species having a CN chain, and therefore the same group 1185-1163 cm^{-1} could also be associated with the oxide species. The Ti-O and O-Ti-O fluorescence emission spectra are derived from a good range of wavelengths between 400 and 800 cm^{-1}. When a TiO$_2$ ion is added to the surface of the TiO$_2$, the catalytic phase changes, and, at an equivalent time, a replacement extraction effect occurs. The broadband is often dropped to 3412.2 cm^{-1} with waterproofing. The height at 1631 cm^{-1} is thanks to the moving sound of the droplets indicating the presence of water-solids.

Table.2: Characteristic Infrared Absorption Region (cm^{-1}) of Diphenylamine.

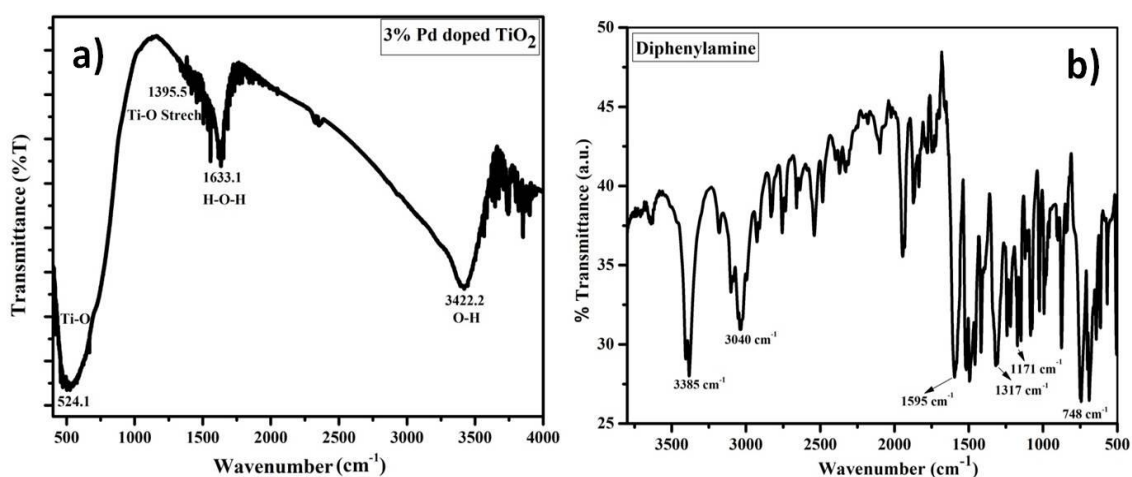| Sl	Region (cm)	Nature of bands	Frequency
1	< 3300	Strong and sharp	C-H present
2	3400-3100	Broad absorption	N-H present (aromatic)
3	1236-1050	Intense-band	C-C or C-N present

Figure.7.a). FT-IR Spectra of a) Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ catalyst b) diphenylamine

3.6 C-N coupling reaction flask

The cylinder has a diameter of 3.6 cm and has a height of 13 cm, and also, the height from the ground is 1.5 cm. The length of the beads should be reduced to the request for breaking two separate sections and a small gap. The surface panel contains a magnetic lock and reactions of mixtures. On a waterproof surface, a coating of catalytic mixture (HC) is applied. The complete catalytic reaction of the HC catalyst is present in the solvent within 110°C hot water bath. The conversion speed of the catalyst is high and then separates the reaction mixture and solvent from the HC catalyst. The photograph of coated honeycomb and coupling reaction as indicated in Figure 8.
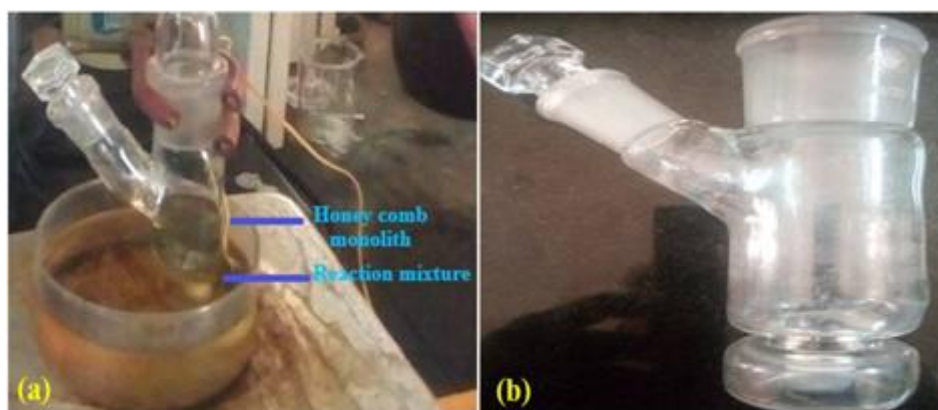
Figure.8. Photographs of a) the reaction mixture and coated honeycomb catalyst.
b) Specially designed reaction flask (reactor) for the C-N coupling reaction.

3.7 Procedure for the C-N coupling reaction

The final product was determined in the bottom flow medium in 25 mL A total of 25 mL around the flak medium dissolve Iodobenzene (200 mg, equivalent to 1), aniline (equivalent 1.5), a catalyst (15 mg), and K$_2$CO$_3$ (equivalent 1). Adding 3 mL of DMF. At a temperature of 110 ^{O}C, their reaction has been preserved. TLC monitors their activities. The reaction was performed 3 times with ether and water. The share of the substrate decided using gas chromatography. The C-N test reaction was presented with a customized reaction. Aryl halides (2 g, 1 equal), Aniline (1.5 in equivalent), and base (1.5 in equivalent) do their thing. A catalyst coating monolith is included in the survey. At 110 ^{o}C, argon was used to treat the reaction. The reaction of TLC was investigated. The couple ether was removed and washed with water 3 times after the reaction to get the solvent absorbed in the surface. The monolith coating is far away from the solvent, washed with water to get rid of the solvent. Then, wash the unheated n-hexane and dry during a warm oven for 2 h^{-1} at 200$\circ$C. an additional two cartridges were looked for the opposite two in response to the C-N reaction. The highest ingredients used are animal ether and ester. The ratios were expressed using TLC to their size. A few sample presentations were identified as ^{1}H NMR, ^{13}C NMR, IR, and multicenter.

3.8 Screening studies

An experimental study of the C-N synthesis of Bromobenzene and Iodobenzene (aryl halide) has been proposed. The powdered powder was utilized in each reaction to recover .0.98 mmol (200 mg) Bromobenzene and 1.5 anilines. 3.7 mol containing 15 mg of catalytic Pd^{2+} ion was used. First, tests are performed where the solvent is added individually to the reaction. Apart from reaction with DMF as a solvent, all other reactions with different solvents are given atoms. The reaction time for toluene blocking was 90 min at 110^{0}C temperature using K$_2$CO$_3$ (1.5 Eqs) because of the base. We tried the inactive response and got the results. Then we use our standard parameters 1.5 equivalents in several settings like CS$_2$CO$_3$, t-BuONa, K$_2$CO$_3$, and C$_6$H$_{15}$N. Their interaction with C$_6$H$_{15}$N and K$_2$CO$_3$ was restricted to the final product, including the copolymers (oxidant) K$_2$S$_2$O$_8$ and T$_B$H$_7$O$_X$, like C$_6$H$_{15}$N. The subsequent step within the analysis is warming up; the reaction was performed at 80◦C, 60◦C, and at temperature, and therefore the extract was kept low temperature and used toluene as a solvent and it's kept as a freezing point, with temperature C$_6$H$_{15}$N as 1.5, and C-N bond as reaction value of 110^{0}C. We tested the response at 1 and 1.5 equivalents for K$_2$CO$_3$ and yielded but about 1.5 of the bottom. Two reactions were conducted with a monolithic catalyst device, a coated monolith, and a 100 mg catalyst containing 50 mg of catalyst. The starting material was used for 2 g of iodobenzene. Both reactions ended with a return of more than 90%. The time it takes for the two reactions to occur is just four hours. The stable, catalytic reaction reacted quickly when the reaction was compared to the powdered material. Finally, we decided to dope 50 mg of monolith cordierite for the further reaction was summarized in Table 3.
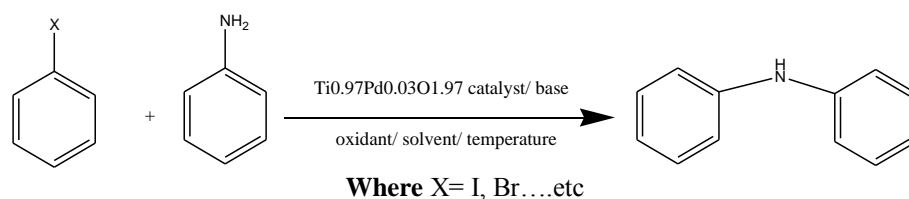

Where X= I, Br….etc

Table.3. Screening of the reaction.

Entry	Base	Oxidant	Solvent	Temp (^{0}C)	Time (hrs)	Yield (%)
1	K$_2$CO$_3$	-	DMF+H$_2$O	100	24	23 [a]
2	K$_2$CO$_3$	Ag$_2$O	DMF+H$_2$O	100	48	-
3	K$_2$CO$_3$	K$_2$S$_2$O$_8$	DMF+H$_2$O	100	24	56 [a]
4	K$_2$CO$_3$	K$_2$S$_2$O$_8$	Toluene+H$_2$O	120	24	53 [a]
5	K$_2$CO$_3$	K$_2$S$_2$O$_8$	Ethenol+H$_2$O	120	24	-
6	K$_2$CO$_3$	K$_2$S$_2$O$_8$	Toluene	120	24	54 [a]
7	K$_2$CO$_3$	K$_2$S$_2$O$_8$	DMF	110	24	67 [a] d
8	t-BuONa	C$_4$H$_6$CuO$_4$	Toluene	120	48	-
9	K$_2$CO$_3$	K$_2$S$_2$O$_8$	Toluene	120	48	46 [a,f]
10	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	12	55 [a,f]
11	K$_2$CO$_3$	-	MeOH+H$_2$O	100	24	-
12	CS$_2$CO$_3$	-	Toluene	110	48	-
13	t-BuONa	K$_2$S$_2$O$_8$	DMF	110	24	35 [a]
14	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	24	42 [a]
15	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	80 [b,b,c]$_1$ d
16	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	40 [a]
17	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	37 [a]
18	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	56 [a]
19	K$_2$CO$_3$	K$_2$S$_2$O$_8$	Toluene	120	24	60 [b,e]
20	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	56 [b,e]
21	t-BuONa	K$_2$S$_2$O$_8$	Toluene	120	48	78 [b,b,c]$_2$ d
22	C$_6$H$_{15}$N	T$_B$H$_7$O$_X$	Toluene	110	04	90 [b,b,c]$_3$ d
23	-	T$_B$H$_7$O$_X$	Toluene	110	48	-

Reaction conditions: 1 equivalent (200 mg) of Bromobenzene [a], Iodotoulene [b], and Iodobenzene b, b, c_1, b, b, c_2, and b, b, c_3. 1.5 equivalent of Aniline[b], 1.5 equivalent of the bottom, 1 equivalent of oxidant, 3 mL of solvent, c_1 and c_2-50mg powder catalyst coated over monolith (5 mg of powder catalyst), and c_3-100mg of catalyst coated over monolith (10 mg of powder catalyst), the temperature at 110 ^{0}C, under Ar atmosphere. All are GC yield. d Isolated yield, [d]100 mg of catalyst coated over catalyst. e0.5 equivalent of the bottom, f_1 equivalent of base.

C-N coupling reaction between iodobenzene and aniline is administered within the presence of $C_6H_{15}N$ base with different solvents are summarized in Table 4. Reaction with Toluene gave >90% yield and DMF solvent gave in Table 3.
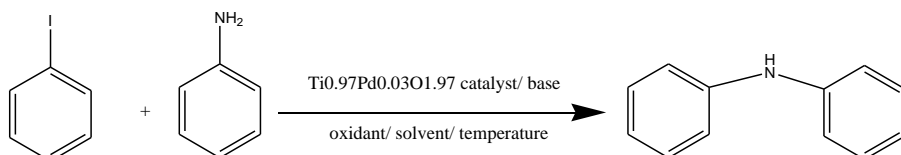
Table.4. Effect of solvents on C-N coupling over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith.

Entry	Base	Solvent	Yield (%)
1	$C_6H_{15}N$	Toluene	**>90**
2	$C_6H_{15}N$	DMF	<45
3	$C_6H_{15}N$	Dioxane	Nil

In Table 3, shows the effect of bases on the C-N coupling reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith. Different bases such as $C_6H_{15}N$, t-BuONa, and K_2CO_3 bases were taken for the comparison. The C-N coupling reaction in the presence of $C_6H_{15}N$ as a base showed >90% conversion and t-BuONa, K_2CO_3 showed around 80% and 70% yield in the Toluene solvent at 110-120°C, reaction condition
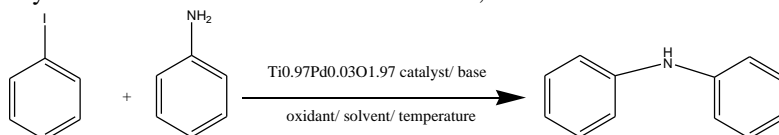
Table.5. Effect of bases on C-N coupling over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith.

| Entry	Solvent	Base	Yield (%)
1	Toluene	$C_6H_{15}N$	**>90**
2	Toluene	t-BuONa	**80**
3	Toluene	K_2CO_3	71

The below Table 6 showed the effect in the presence and absence of different oxidants, bases, and solvents on the C-N coupling reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith. , in the presence of $T_BH_7O_X$ as oxidant with $C_6H_{15}N$ as base and Toluene as solvent condition gave >90% of yield and $K_2S_2O_8$ as an oxidant with K_2CO_3, t-BuONa as bases gave >65%, >75% respectively.
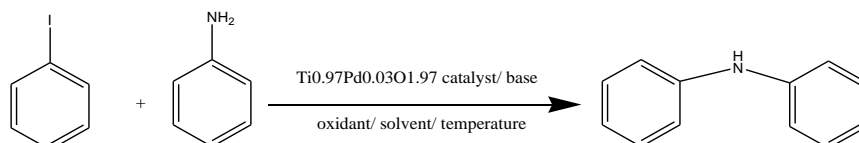
Table.6. The effect the presence and absence of different oxidants, bases, and solvents on the C-N coupling reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith.

Entry	Base	Oxidant	Solvent	Yield (%)
1	K$_2$CO$_3$	K$_2$S$_2$O$_8$	DMF	**>65**
2	t-BuONa	K$_2$S$_2$O$_8$	Toluene	**>75**
3	t-BuONa	-	Toluene	Nil
4	C$_6$H$_{15}$N	T$_B$H$_7$O$_X$	Toluene	**>90**
5	C$_6$H$_{15}$N	-	Toluene	Nil
6	K$_2$CO$_3$	-	DMF+H$_2$O	. >20
7	CS$_2$CO$_3$	-	Toluene	Nil
8	K$_2$CO$_3$	Ag$_2$O	DMF+H$_2$O	Nil
9	K$_2$CO$_3$	T$_B$H$_7$O$_X$	Dioxane	Nil

In the absence of bases with the presence of different oxidants with different solvents are carried out, the C-N coupling reaction gave a less amount of yields, such as 57% and 27% yield, respectively.
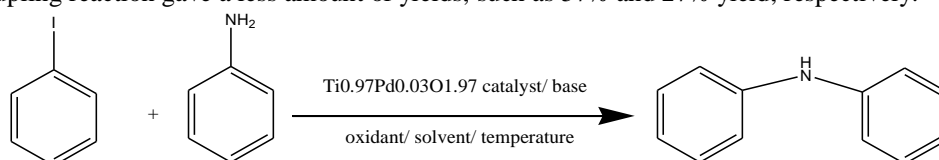
Table.7. The effect in the presence of oxidant and absence of base on C-N coupling over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ Coated monolith.

Entry	Oxidant	Solvent	Yield (%)
1	T$_B$H$_7$O$_X$	Toluene	**57**
2	K$_2$S$_2$O$_8$	Toluene	**27**

The study was conducted to study the possibility of Buchwald-Hartwig catalyzing the reaction standard set at 110 °C. The product was observed within the presence of species, the reaction performed well and yielded the identical final product with 93% yield. The concentration dropped as low as 0.03 mol%. The input product ranges from 0.01 to 0.3 mol percent to decide whether an increase in the pore polarity contributes to any difference in yield. However, the extract yield did not increase significantly. The reactions with diverse solvents, including H$_2$O, toluene, 1, 4 dioxane, p-xylene, and hexane, were performed under the best conditions to build the simplest catalysts. The most important active yield is toluene among other things, but in water and hexane reactions it does not precede at least. As a rule, the foremost common product was found to be t-BuONa (between Na$_2$CO$_3$, K$_2$CO$_3$, and CS$_2$CO$_3$).

3.9 Substrate scopes

The yields of aryl halides and amines were used for the replacement of C-N behavior listed in Table 2. We have used the simplest conditions which are like aryl halide (2 g), 1.5 particle size amines, 1.5 equivalent C$_6$H$_{15}$N as a table.8. containing T$_B$H$_7$O$_X$ oxidant with 20 ml of Toluene as a solvent. Nearly 50 mg of catalyst and cordierite monolith were coated with any reaction to the catalyst. The aryl iodide derivatives showed good reactivity at the final amines products providing electrical excitability and diffraction contributions. All products are isolated and located to be analyzed by ^{1}H NMR and ^{13}C NMR. The result has been widely accepted for the utilization of amines and amines. The reaction with aryl iodide was inhibited by yielding a positive yield compared with aryl bromide.

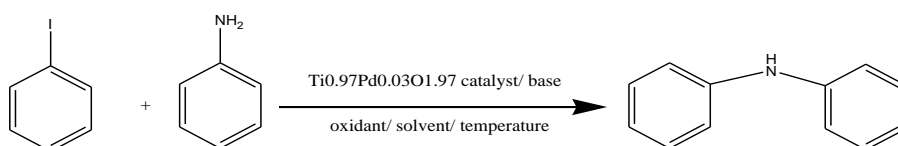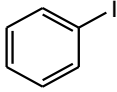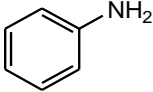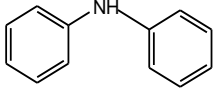3.10 C-N coupling of aniline with aryl iodides and aryl bromides.
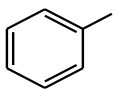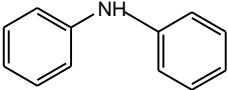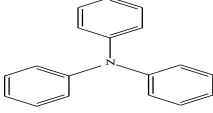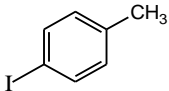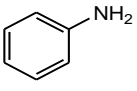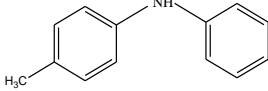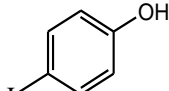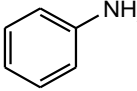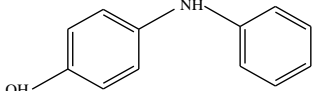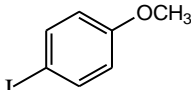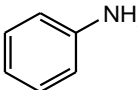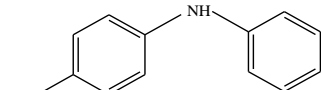
Table.8. The substrate scope of the reaction.

Entry	Aryl halides	Amines	Product	Time (h)	Yield (%)	TOF (h^{-1})
1	(iodobenzene)	(aniline, NH₂)	(N-phenylaniline, NH)	4	93	5.90
2	(iodobenzene)	(diphenylamine, NH)	(triphenylamine)	8	90	2.86
3	(4-iodotoluene, CH₃)	(aniline, NH₂)	(4-methyl-N-phenylaniline)	12	72	1.52
4	(4-iodophenol, OH)	(aniline, NH₂)	(4-hydroxy-N-phenylaniline)	5	65	4.32
5	(4-iodoanisole, OCH₃)	(aniline, NH₂)	(4-methoxy-N-phenylaniline)	7	80	2.90

Reaction condition: 1 aryl halide equivalent (2 g), 1.1 aniline equivalent, 1.5 base $C_6H_{15}N$ equivalent, 20 mL solvent of Toluene, 50 mg honeycomb monolithic catalyst, 120 hrs °C temperature and Ar atmosphere, All is alone. TOF = [(Product moles no./ Catalyst active site moles no.)] per hour. This complete reaction is given in bold. To demonstrate the goodness of the Pd doped TiO₂ catalyst, the C-N reaction (Buchwald Hartwig) was performed using deactivated (electron-rich) aryl iodides and bromides. The results are summarized within the Table.8. The data demonstrated that the product was highly successful for 8-18 hours (75-93 percent). Aryl iodides (I, Br) inhibit the transportation of electronics and provide high-dose related products (92–96%) with the corresponding yield of the electron (75%–84%) for aryl iodides. Ortho substitutes low concentrations (62-66%) and aniline for aryl halides. However, iodobenzene exhibits better results than natural, water-soluble bromobenzene products, such as amine products. These compounds have been described as melting point of solvent, ¹H-NMR, and ¹³CNMR and have agreed to conversion and recombining of aniline and iodobenzene following reaction with the additional literature; the reaction mixture is dissolved. Rinse it with acyl acetate before purification to remove the detergent and finally dry it. The propeller had not been well packed until the third cycle. It was found EDX and FE-SEM analyses were carried out after the third cycle to verify the validity of the search. The data indicate the quality of the Pd test obtained from the thermal test is preserved by the manufacturer to determine, if a Pd is involved in any solid material. When the reaction is complete, the bed rotates across the Celite bed to allow the unwanted agent to remain behind the bed. For a substitute reaction, the filtrate was reactivated with the reaction mixture of an equal size without any addition to the identical reaction. The study was studied GC, which reveals that the confirmation of the products.

IV.   RECYCLING OF THE CATALYST

We have developed a protocol for the supplier. Iodobenzene (2 g) and Aniline (1.5 eq.) Were considered as starting materials using standard standards. Reinforcement of the $Ti_{0.97}Pd_{0.03}O_{1.97}$ Monolith Compound: After the reaction was performed, the electron microscope Monolith was removed and continued to the third unsaturated phase (Figure 9). $Ti_{0.97}Pd_{0.03}O_{1.97}$ was purified with hexane water, and the DMF and K_2CO_3 were purified with water. Monolith is frozen at 110 ^{0}C and was used in new reactions. There is no significant loss and a significant role for the Iodobenzene reaction and aniline, which are summarized in the below table. Even after the 6th cycles of the C-N coupling reaction over $Ti_{0.97}Pd_{0.03}O_{1.97}$ coated monolith, the yield obtained 99% in 6h. This indicates that the $Ti_{0.97}Pd_{0.03}O_{1.97}$ catalyst is not deactivating. The regenerative designs of the HC monolith catalyst are shown in Figure 5. After each color, the monolith employed by the reaction is quenched then washed with water to get rid of the stain, then wont to purify the impurity. The washed monolith was heated during a preheated oven at 200 ° C for two hours at temperature. The lump was reheated to offer more reaction. We got 100% resuscitation up to 6th, but within the 7th round, we've reduced yields by 85%. Manufacturer's Recycling Chart. Their response time within the 6th cycle was 1 to three steps, and therefore the

response time was 4 hours. The TOF concentration after ten cycles of the reaction was 5090 h^{-1}. Also, for the reconstruction and remodeling of an activator, the reaction was selected between aniline and Iodobenzene (Table 4). After performing the reaction, the reaction mixture was dissolved to separate the pure catalysts; the ethyl solvent were washed and later heated within the period before regeneration. The catalytic tests were repeated for 10 cycles for palladium precursors to check the sturdiness and effectiveness of the powder. The reactor was collected from the reaction employing a 100% reaction mixture within the first cycle. The yield of the 10 cycle system is slower than the primary phase and should end in the disruption of the molecules and therefore the loss of the source. Additionally to the present, after separation, it washed with water, which helps with the filters and results in final products.
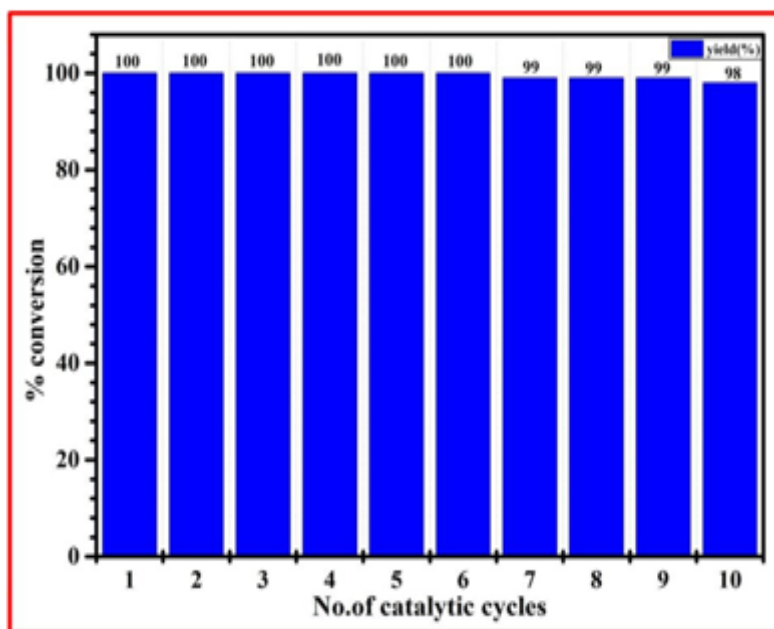

Figure.9. Recycling of the catalyst by employing standard reaction conditions. Several cycles of the C-N coupling reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{1.97}$ coated monolith (time-4h).

V.   CHARACTERIZATIONS OF AMINE DERIVATIVES

5.1 NMR studies
1H NMR (CDCI3 200 M Hz) 8 5.68 (s, IH), 6.92 (t, J= 8Hz, 2H), 7.06 (d, J= SMz, 4H), 7.26 (t, J= SMz, 4H)
13C NMR (C D C I3 125 M Hz) 6 117.7, 120.8, 129.2, 143.0
IR: 3383 cm ''N-H stretching (aromatic secondary amine) 1319 cm'' C-N stretching of secondary amine.
.5.2 Diphenylamine.
Purification by flash chromatography (hexanes: ethyl acetate=10:1) gave 200.2 mg of white crystals (0.465 mmol, 93%) [57]. 1H NMR: δ 5.70 (s, br, 1H), 6.993-6.951 (m, 2H), 7.092-7.097 (m, 4H), 7.260-7.332 (m, 4H). 13C NMR: δ 115.2, 118.4, 129.3, 146.4.

5.3 Triphenylamine.
Purification by flash chromatography (hexanes: ethyl acetate=10:1) gave 200.1 mg of white crystals (0.465 mmol, 90%). 1H NMR: δ 6.94-6.97 (m, 3H), 7.08-7.087 (m, 6H), 7.30-7.26 (m, 6H). 13C NMR: δ 118.04, 121.2, 129.5, 143.4 [58].
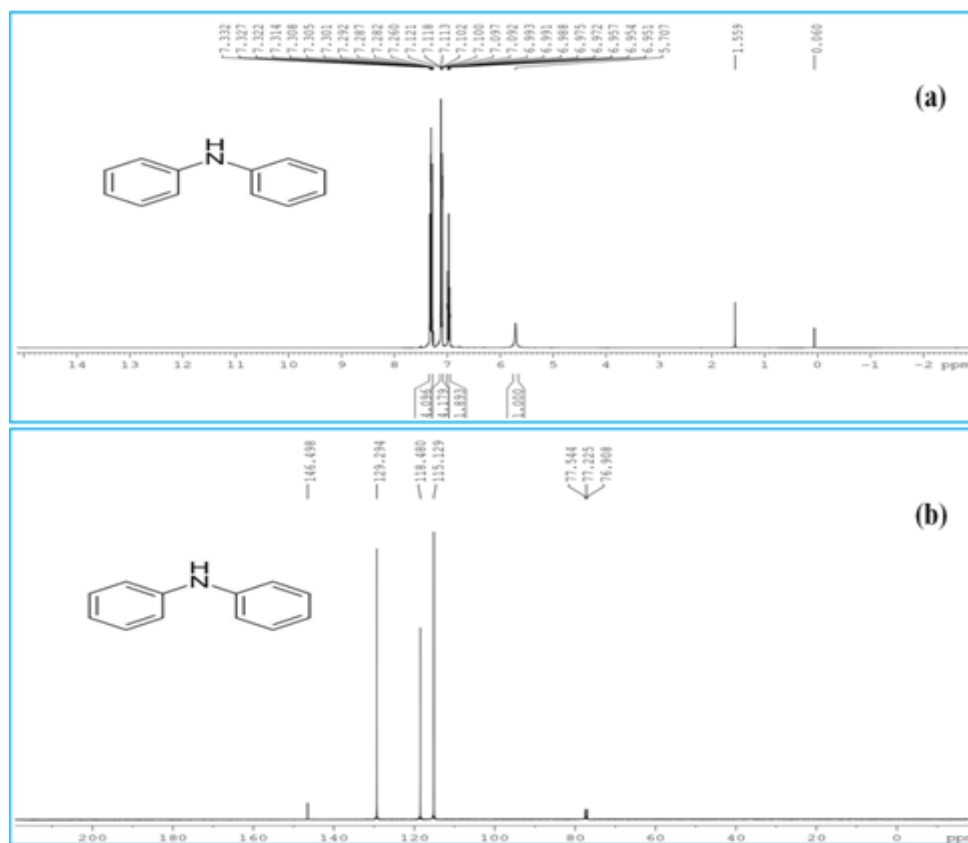
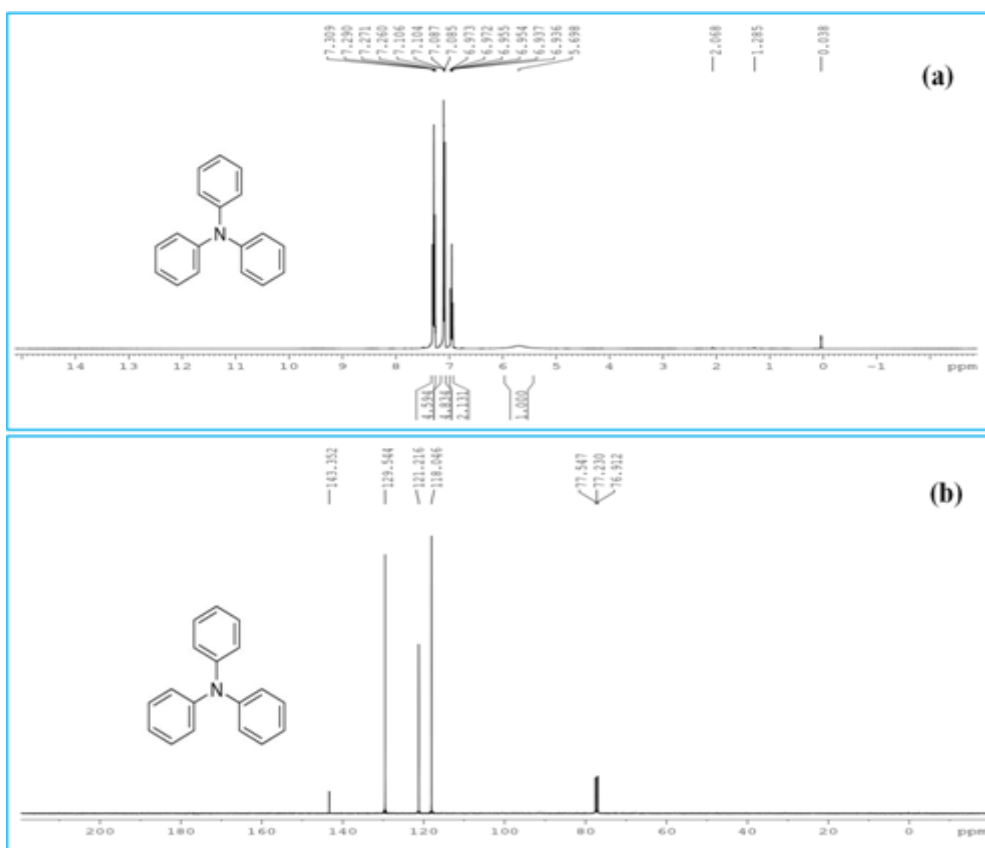**Figure.11.a) ¹H NMR and b) ¹³C NMR spectra of Diphenylamine. In CDCl₃**

Figure.12 a) ¹H NMR and b) ¹³C NMR spectra of Triphenylamine in CDCl₃.

VI.   CONCLUSION

In summary, we have established a new class of TiO_2 and Pd doped TiO_2 catalysts for the C-N coupling reaction. This method is environmentally friendly without using any toxic catalyst or reagents. This reaction allows a diversity of functional groups. Reactions were done using catalyst coated over cordierite monolith by a sole method and also useful for recovering the catalyst.

ACKNOWLEDGMENT

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