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Research Article

Cu/Pd Bimetallic Supported on Mesoporous TiO_2 for Suzuki Coupling Reaction

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Abstract

Generally bimetallic catalysts are more superior to monometallic catalysts and provide a better platform for the development of novel catalysts with enhanced activity, selectivity, and stability. In the current work we have prepared Cu/Pd bimetallic supported on mesoporous TiO_2 by hydrothermal method. The prepared system was characterized by various physico-chemical techniques such as XRD, TG-DTG, SEM, EDAX, BJH isotherm, and XPS. Thermal stability and complete electronic structure were identified from TG and XPS measurements respectively. The bimetallic system was found to be very active in Suzuki cross-coupling reaction using different substrates. The products were separated and purified by column chromatography and the resultant products were characterized thoroughly by ^1H NMR, and FT-IR analysis. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Cu/Pd-TiO_2; Suzuki Reaction; Biphenyl, 4-Nitrobiphenyl; Heterogeneous Catalysis

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1. Introduction

Palladium is the most versatile and useful metal for various carbon-carbon bond forming reactions. Among various coupling reactions, palladium catalyzed Suzuki cross-coupling reaction between an organic halide and an organoboron compound has become the most powerful strategy for the construction of carbon-carbon bonds [1]. This particular reaction is extremely important for the generation of biaryl moieties which are the major building blocks of varieties of compounds such as herbicides, pharmaceuticals, natural products, polymers, etc. [1-5]. The major advantage of Suzuki coupling reaction is the mild reaction condition and organoboronic acids, an inevitable part of Suzuki coupling reaction are stable, easily available, environmentally benign, cost effective and non-toxic [6]. Extensive work has been carried out on Suzuki coupling reaction in a homogeneous way, however it suffers from number of drawbacks such as catalyst decomposition, poor reagent solubil-

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ity, etc. Heterogenization of palladium catalyst is a promising option to produce effective, recyclable and stable heterogeneous catalysts for Suzuki coupling reaction [7,8]. Leaching of the active component palladium from the support is a very serious problem in heterogeneous catalysis that may affect the overall efficiency of the reaction. So, it is very necessary to fabricate a heterogeneous catalyst with good stability, activity and selectivity. Support is an indispensable part of heterogeneous catalysts and here we selected cost effective, stable and environmentally benign mesoporous TiO_2 as the support for bimetallic catalytic system. The deposition of noble metal nanoparticles on the support used as catalysts is attracting immense attention because of the widespread use of these particles in heterogeneous catalysis [9]. There have been a lot of reports for palladium loaded on different supports, such as dendrimers [10,11], magnetic nanoparticles [12,13] and mesoporous silica [14,15] for Suzuki coupling reaction. Nowadays a few reports are there on supporting noble metal nanoparticles (NPs) on Metal-organic frameworks (MOFs) for Suzuki–Miyaura coupling reaction [16].

Bimetallic catalysts, composed of two metal elements in either alloy or intermetallic form, often emerge as materials of a new category with catalytic properties is different from monometallic catalysts, depending on the composition and size/morphology. Bimetallic catalysts have unique properties which are superior to ordinary materials and therefore provide a better platform for the development of novel and efficient catalysts. Recent studies are focused to enhance the activity, selectivity, and stability of the catalysts used as well as elucidating the catalytic reaction mechanisms by designing a variety of novel Pd-based bimetallic materials. Chen *et al.* prepared and evaluated the alloy and the core-shell Au-Pd particles confined in silica nano rattles in order to enhance the properties of catalysts for the Suzuki coupling reaction [17]. A highly active catalyst based on Pd-Co alloy nanoparticles supported on polypropylenimine grafted on graphene could effectively carried out Sonogashira coupling reaction, reported by Shaabani *et al.* [18]. Choi *et al.* synthesized a variety of carbon-supported bimetallic Pd-M (M = Ag, Ni, and Cu) nanoparticles by γ-irradiation at room temperature, and the resulting Pd-Cu/C nanoparticles exhibited high catalytic efficiency in the Suzuki- and Heck-type coupling reactions [19]. Gao *et al.* reported the effectiveness of montmorillonite supported Pd-Cu for Sonogashira coupling reaction [20].

Here, we report the Suzuki coupling reaction by using Cu/Pd bimetallic supported on mesoporous TiO_2. Various parameters such as effect of catalysts, effect of solvents, effect of substrates and effect of bases were evaluated for the same. Photocatalysis by Cu/Pd on titania is common, but thermal catalysis by Cu/Pd supported on mesoporous titania is rare and also we have done extensive work on various parameters which influence the Suzuki coupling reaction.

2. Materials and Methods

$Ti[OCH(CH_3)_2]_4$ (97 %), $PdCl_2$ (99 %), and $Cu(NO_3)_2.3H_2O$ (99 %) were used as obtained from Sigma Aldrich, Germany. All the solvents such as N,N-dimethylformamide, dimethyl sulfoxide, 1,4-Dioxane, ethanol, acetic acid, etc. were purchased from Merck Pvt. Ltd, India with more than 99 % purity. Structure, crystalline nature and lattice parameters of the catalyst was identified by X-ray diffraction analysis. Crystallite size of the sample was calculated by Scherrer's formula. The powder X-ray diffraction of the sample was performed using a Bruker AXSD8 diffractometer with Ni filtered Cu-Kα radiation source (λ = 1.5406 A°) in the range of 10-70° at a scan rate of 0.5°/min. Thermal stability, decomposition temperature, phase change, etc. were identified by thermal analysis. Thermal analysis was done using a Perkin Elmer Pyris Diamond thermo gravimetric/differential thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C. SEM was used to understand the morphology of the sample. Compositional analysis was carried out by EDAX using JEOL Model JED-2300. SEM micrographs were taken using JEOL Model JSM-6390LV with a resolution of 1.38 eV.

Surface area and porous nature of the catalyst was determined by Micromeritics Tristar 3000 surface area analyzer. Surface composition and electronic structures were analyzed by X-ray photoelectron spectroscopy using an Omicron Nanotechnology XPS system with a monochromatic Al Kα radiation ($h\nu$ = 1,486.6 eV) of source voltage 15 kV and emission current of 20 mA. All scans were carried out at ultrahigh vacuum of 2×10^{-10} mbar. The obtained XPS spectra were de convoluted using Casa XPS program, (Casa Software Ltd, UK), in which the background was simulated using the Shirley function and the peaks were fitted using a Gaussian-Lorentzian function. All binding energies were referenced to C1s for calibration. ^{1}HNMR (400 MHz; $CDCl_3$) was used to characterize the isolated products.

2.1 Preparation of the catalyst

Cu/Pd bimetallic TiO_2 was prepared by hydrothermal technique. The 10 mL of $Ti[OCH(CH_3)_2]_4$ was dissolved in 30 mL of ethanol/acetic acid (1:1 v/v) mixture by vigorous stirring at room temperature. To this 0.23 g of $PdCl_2$ in 20 mL of 1:1 v/v of water/acetic acid and 0.09 g of $Cu(NO_3)_2.3H_2O$ in 50 mL water were added and the whole mixture was sonicated for about 5 h to form a clear solution. After proper aging, the obtained Gel was transferred to a stainless steel autoclave with 500 mL capacity having Teflon lining. This was heated at a temperature of 110 °C for 12 h. The whole mixture was washed several times with various solvents to remove the impurities completely. The obtained powder was dried at 80 °C and calcined at 500 °C for 3 h to get the desired Cu(1wt%)-Pd(4wt%)-Ti system. We have prepared various bimetallic catalysts by varying the concentration of dopants. Monometallic Cu-TiO_2 and Pd-TiO_2 were also prepared by the same procedure as discussed above.

2.2 Suzuki coupling reaction

Aryl halide (3 mmol), phenyl boronic acid (3.6 mmol), and base (9 mmol) was taken in a 10 ml Round Bottom flask and to this fixed quantity (0.1 g) of catalyst was added followed by the solvent. The whole mixture was stirred under reflux temperature. The reaction progress was monitored by Thin Layer Chromatography using hexane:ethyl acetate (10:1) as eluent. After 20 hours, the catalyst was recovered by filtration and washed several times with various organic solvents. Then the organic layer was separated out with the help of a separating funnel and the pure compound was isolated by column chromatography using hexane:ethyl acetate (10:1) as the mobile phase.

3. Results and Discussion

3.1 X-ray diffraction

Figure 1 represents the XRD pattern of Cu(2wt%)-Pd(4wt%)-Ti system. Sharp and intense peaks after calcination at 500 °C represent the highly crystalline nature of the material. Here the dominant phase is anatase with major angle at $2\theta = 25.3°$ (JCPDS card no. 21-1272). The peaks corresponding to Pd and Cu were also absent due to their marginal concentration. Crystallite size of the sample was calculated from Scherrer equation by using full width at half maximum (FWHM) of the (101) peak of the anatase phase. The average crystallite size was calculated to be 18.1 nm. Here the crystallite size was found to be high due to the agglomeration of particles.

3.2 Thermal analysis

Thermal analysis is used to understand the stability of the prepared catalyst. Figure 2 represents the TG and DTG curves of Cu/Pd-Ti system. A weight loss around 100 °C may be due to the loss of adsorbed water. Three weight losses located below 460 °C is due to the complete decomposition of precursors. After 460 °C, there is no noticeable weight loss on DTG, which indicates the stability of the catalyst and hence the calcination temperature was fixed at 500 °C.

3.3 Scanning electron microscopy

From the SEM images, we could understand that, all the particles are irregular in shape.

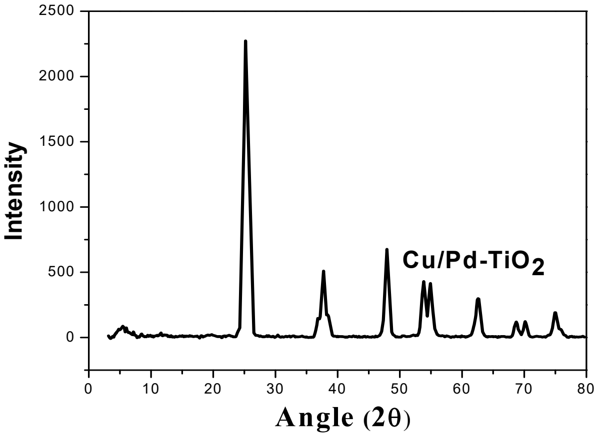

Figure 1. XRD pattern of Cu-Pd-TiO_2 system

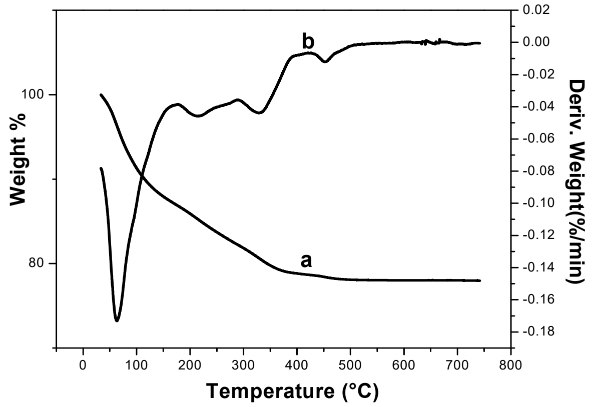

Figure 2. a) TG and b) DTG curves of Cu(2wt%)-Pd(4wt%)-TiO_2 system

The shapeless structures in the image are mainly due to agglomeration and that would have happened during hydrothermal synthesis. Irregularity of Cu(2wt%)-Pd-Ti system was high due to higher concentration of Cu compared to Cu(1wt%)-Pd-Ti. Particle aggregation results in an increase of particle size thereby decreasing the surface area.

3.4 Energy dispersive X-ray analyses

Energy Dispersive X-ray analysis is a qualitative technique used to estimate the percentage of elements present in the prepared system. The intensity of the peak is directly related to the concentration of elements. EDX spectrum of Cu/Pd bimetallic TiO_2 with different concentration of copper is shown in Figures 5 and 6. Spectra showed the presence of Cu and Pd along with Ti and O. So, EDX give a qualitative idea about the composition of the system. The atom percentages of impurities are tabulated in Table 1.

3.5 X-ray photoelectron spectroscopy (XPS)

Figures 8, 9, 10, and 11 show the high resolution scan over various core levels of Cu(2wt%)-Pd-Ti system, such as: Ti2p, O1s, Pd3d, and Cu2p, respectively. Peaks observed at 458 eV and 464 eV due to spin orbit splitting corresponds to the $Ti2p_{3/2}$ and $Ti2p_{1/2}$ levels confirmed Ti^{+4} species. O1s signal at 528.1 eV indicates O^{2-} ion in the lattice of TiO_2. The binding energy values of $Pd3d_{5/2}$ (334 eV) and $3d_{3/2}$ (341 eV) revealed that palladium was in the form of Pd(0) in the prepared system. Peak

Table 1. Atom percentage of impurities present in Cu-Pd-Ti System

Name of the catalyst	Atom % of impurities	
Cu(1wt%)-Pd-Ti	Cu-1.9	Pd-3.9
Cu(2wt%)-Pd-Ti	Cu-2.6	Pd-4.1

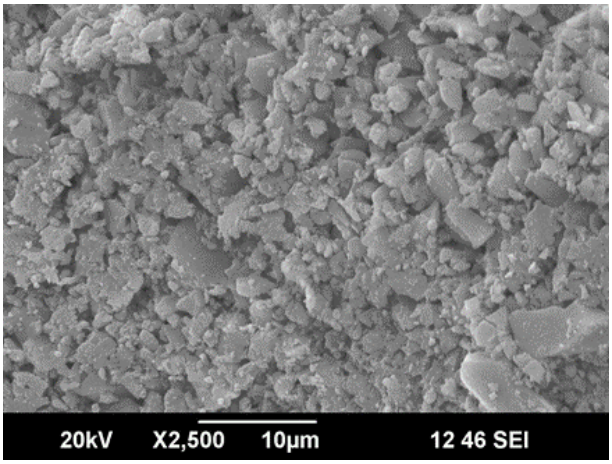

Figure 3. SEM image of Cu(1wt%)-Pd-Ti

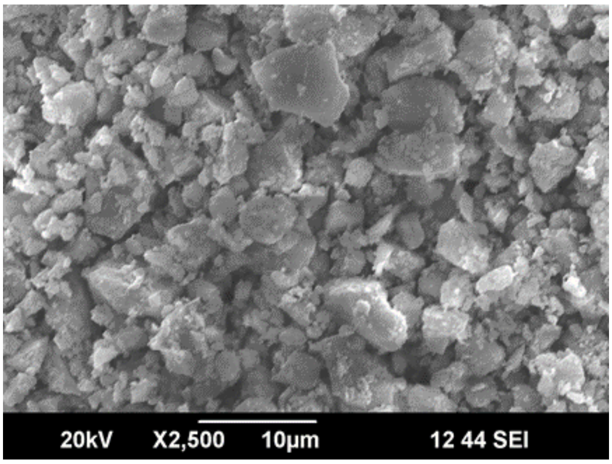

Figure 4. SEM image of Cu(2wt%)-Pd-Ti

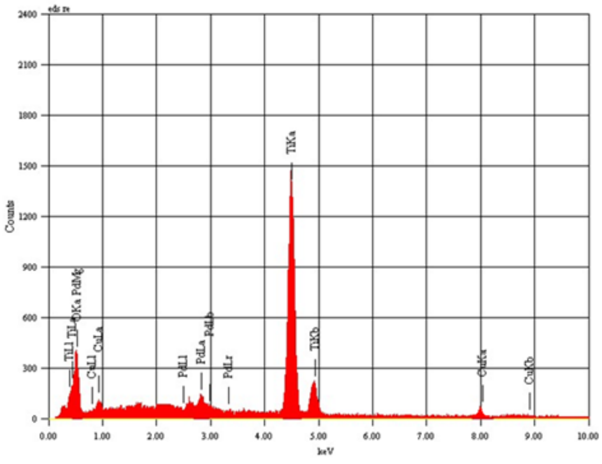

Figure 5. EDX spectrum of Cu(1wt%)-Pd-Ti

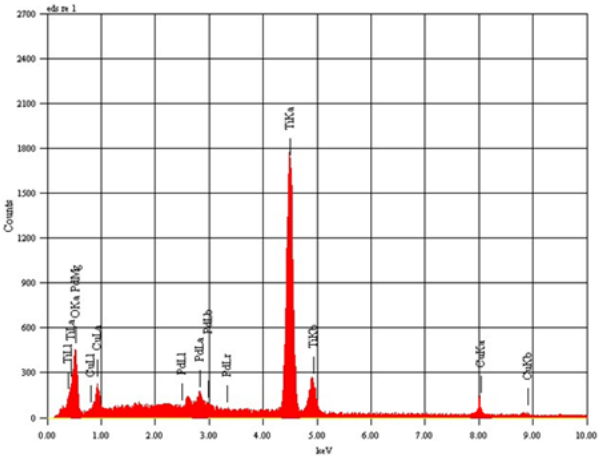

Figure 6. EDX spectrum of Cu(2wt%)-Pd-Ti

at binding energy of 932 eV corresponds to $Cu2p_{3/2}$ and another peak at 952 eV with a binding energy difference of 20 eV represents $Cu2p_{1/2}$ confirmed the presence of Cu(II) species. These two peaks indicate the good dispersion of metal into TiO_2 matrix.

3.6 BJH isotherm

The adsorption/desorption isotherm of bimetallic catalyst is shown in Figure 7. The catalytic system follows type IV isotherm with hysteresis loop at a relative pressure range of (p/p0) 0.65-1.H1 hysteresis observed in the figure is the typical characteristic of mesoporous material. This is also used to calculate the BET surface area, pore volume and pore diameter of the prepared system. The BET surface area was found to be 60 m^2/g. Pore volume and pore diameter of the concerned system was calculated to be 2.49 cm^3/g and 43.8 Å, respectively.

3.7 Catalytic activity studies

Transition-metal catalyzed cross-coupling reactions are powerful tools for the formation of new carbon–carbon bonds, which has got immense significance in industrial as well as synthetic points of view. Extensive work has been carried out on Suzuki coupling reaction in a homogeneous way, however, it suffers from a number of drawbacks, such as: catalyst decomposition, poor reagent solubility, etc. In this work, we made an attempt to evaluate the activity of Cu/Pd-Ti catalyst in Suzuki coupling reactions. Reaction scheme is shown in Figure 12.

Five different catalysts were employed to carry out Suzuki coupling reaction. The results are shown in Table 2. A marginal yield was obtained with catalyst having 1 wt% of Copper. But the product yield was increased to 21 %, as the concentration of the copper increased. Monometallic Pd(4wt%)-Ti system showed bet-

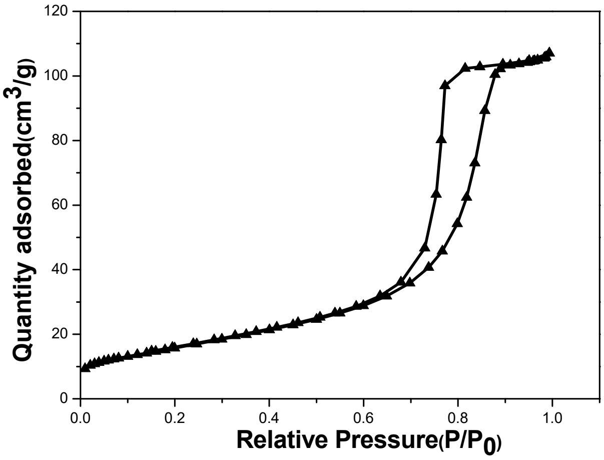

Figure 7. BJH isotherm of Cu(2wt%)-Pd-Ti

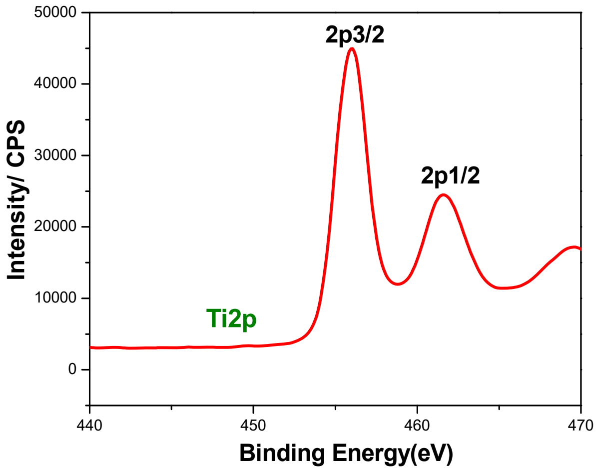

Figure 8. Ti2p levels of Cu(2wt%)-Pd-Ti

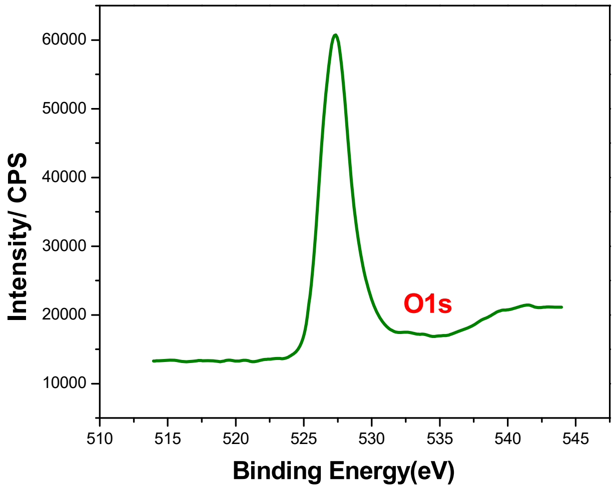

Figure 9. O1s level of Cu(2wt%)-Pd-Ti

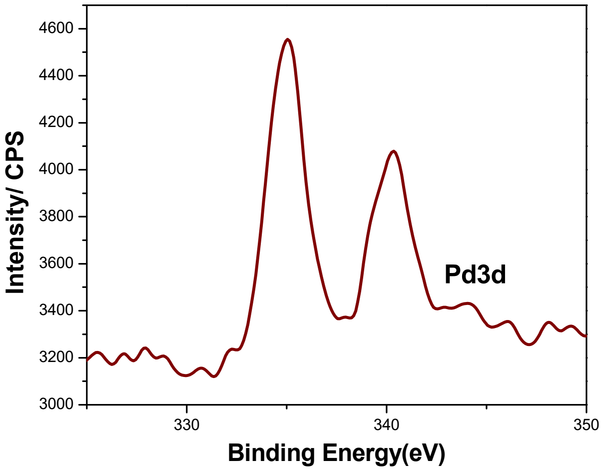

Figure 10. Pd3d core levels of Cu(2wt%)-Pd-Ti

ter activity compared to Copper modified TiO_2, because 'Pd' is the active component in the catalytic system. Around 52 % yield was obtained with monometallic Pd modified TiO_2 system. Combination of Cu and Pd on TiO_2 improved the product yield, which unambiguously proved the effectiveness of bimetallic catalytic system. The incorporation of Cu and Pd is clearly evidenced from XPS results. Mesoporous nature of the support can be seen from BJH adsorption isotherm, which firms both the metals perfectly. High concentration of promoter enhances the activity of Cu(2wt%)-Pd(4wt%)-Ti, which is evidenced from EDX as well as XPS results. In the bimetallic system, copper acts as a promoter which alters the rate of the reaction and also improves the selectivity towards a particular product. Synergistic effect due to Pd and Cu is also responsible for the improved activity of bimetallic systems. From the table, it is clear that Cu(2wt%)-Pd(4wt%)-Ti system was superior to other catalysts and produced around 75 % of the product biaryl using DMF as the solvent. We have again checked the activity of the three effective catalysts by varying water as the solvent. Here also the results followed the same pattern and around 62 % of biaryl was obtained with Cu(2wt%)-Pd(4wt%)-Ti catalytic system. The results are presented in Table 3.

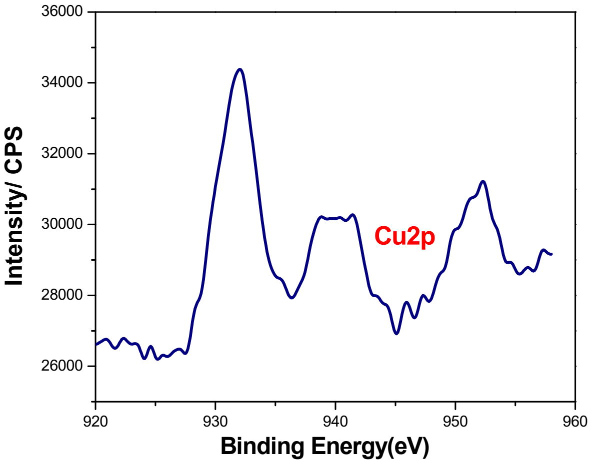

Figure 11. Cu2p levels of Cu(2wt%)-Pd-Ti

Table 2. Suzuki coupling reaction using different catalysts

Catalysts	% Yield
Cu(1wt%)-Ti	11
Cu(2wt%)-Ti	21
Pd(4wt%)-Ti	52
Cu(1wt%)-Pd(4wt%)-Ti	63
Cu(2wt%)-Pd(4wt%)-Ti	75

Reaction Conditions: Bromobenzene (3 mmol), Phenyl boronic acid, (3.6 mmol), K_2CO_3 (9 mmol), Temperature (90 °C), DMF (10 mL), ReactionTime (20 hours), Catalyst amount (0.1 g)

Suzuki coupling reaction was carried out in polar protic, polar aprotic, and non-polar aprotic solvents in order to understand its influence on this reaction. The results are summarized in Table 4. Compared to non-polar solvents, good results were obtained with polar solvents. Smooth interaction between the substrates and the active sites of the catalyst takes place very effectively in polar solvents due to its easier diffusion effect compared to non-polar solvents. That is why yield of the product biaryl was found to be higher with polar solvents. Among different solvents, dimethyl formamide (DMF) showed higher yield of around 75 % using Cu(2wt%)-Pd(4wt%)-Ti as the catalytic system. Poor yield of around 28 % was obtained with non-polar aprotic solvent xylene. Poor reagent solubility and lesser interaction between the substrate and catalytic active site results in poor yield. The results are tabulated in Table 4. We have again checked the activity only in polar solvents using Cu(2wt%)-Pd(4wt%)-Ti by varying the base as NaOH.

Table 3. Effect of three active catalysts in Suzuki reaction using water as the solvent

Catalyst	% Yield
Pd(4wt%)-Ti	41
Cu(1wt%)-Pd(4wt%)-Ti	53
Cu(2wt%)-Pd(4wt%)-Ti	62

Reaction conditions: Bromobenzene (3 mmol), Phenyl boronic acid, (3.6 mmol), K_2CO_3 (9 mmol), Temperature (90 °C), Water (10 mL), Time (20 hours), Catalyst amount (0.1 g)

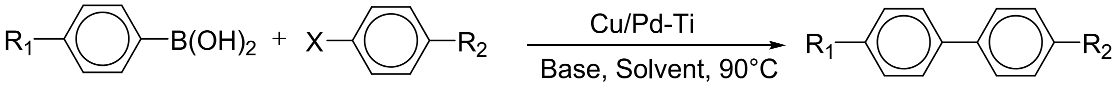

Figure 12. Reaction scheme for Suzuki Coupling reaction catalyzed by Cu-Pd-Ti system

Here the activity followed the same pattern as before and higher yield (61 %) was obtained with DMF as the solvent. The results are summarized in Table 5.

Base is an inevitable part of Suzuki reaction. Without the presence of a base, these reactions are not feasible. Boron containing compounds can be activated in the presence of a base, and also facilitate the formation of R1Pd-OR from R1Pd-X. But exact understanding of this parameter is still unclear. We have tried four different bases to understand its effect on Suzuki reaction. The yield was different with different bases. Higher yield of around 75 % was obtained with Cu(2wt%)-Pd(4wt%)-Ti system using K_2CO_3 as the base and poor yield was obtained with triethyl amine. The results are presented in the Table 6.

Different substrates were tried in order to find out the effect of this one on Suzuki coupling reaction. The electronic factors of substrates had no considerable effect on the reaction. For electron releasing and electron withdrawing substituent, we got a comparable yield. The results are tabulated in Table 7.

We have conducted the recycling studies by washing the Cu(2wt%)-Pd(4wt%)-Ti using different solvents and then calcined at 500 °C for 1 hour. No significant loss of catalytic activity was observed after three cycles. The results are shown in Table 8.

3.7 Mechanistic details of Suzuki coupling reaction

Oxidative addition, transmetallation and reductive elimination are the three major steps involved in Suzuki coupling reaction [21]. Oxidative addition can be considered as the rate determining step in this catalytic cycle [22]. The aryl halide reacts with copper present in the Cu-Pd-Ti system giving aryl copper halide in the first step which upon transmetallation gave aryl palladium halide [23,24]. This Ar-Pd-X reacts with Ar-B(OH)$_2$ to give Ar-Pd(II)-Ar and XB(OH)$_2$. This trans Ar-Pd(II)-Ar undergoes reductive elimination gives the product and regenerates Pd(0) catalyst, which can actively participate in other catalytic cycles. The reaction proceeds with complete retention of stereochemistry for alkenyl halide and with inversion for allylic and benzylic halides. The re-

Table 4. Effect of solvents on Suzuki coupling reaction

Solvents	% Yield
DMF	75
Dioxane	59
DMSO	39
Water	65
Ethanol	70
Acetic acid	56
Toluene	32
Xylene	28

Reaction conditions: Bromobenzene (3 mmol), Phenyl boronic acid (3.6 mmol), K_2CO_3 (9 mmol), Catalyst used (Cu(2wt%)-Pd(4wt%)-Ti, Temperature (90 °C), Solvent (10 mL), Time (20 hours), Catalyst amount (0.1 g)

Table 5. Effect of polar solvents on Suzuki coupling reaction

Solvents	% Yield
DMF	61
Ethanol	49
Water	51

Reaction Conditions: Bromobenzene (3 mmol), Phenyl boronic acid (3.6 mmol), NaOH (9 mmol), Catalyst used (Cu(2wt%)-Pd(4wt%)-Ti, Temperature (90 °C), Solvent (10 mL), Time (20 hours), Catalyst amount (0.1 g)

Table 6. Effect of bases on Suzuki coupling reaction

Base	% yield
K_2CO_3	75
Na_2CO_3	67
KOH	57
Et_3N	61

Reaction conditions: Bromobenzene (3 mmol), Phenyl boronic acid (3.6 mmol), Base (9 mmol), Catalyst used (Cu(2wt%)-Pd(4wt%)-Ti, Temperature (90 °C), DMF (10 mL), Time (20 hours), Catalyst amount (0.1 g)

Table 7. Effect of substrates on Suzuki coupling reaction

Sl No.	R1	R2	Base	%Yield
1	H	H	K_2CO_3	75
2	H	CH_3	K_2CO_3	77
3	H	NO_2	K_2CO_3	73

Reaction conditions: Bromobenzene (3 mmol), Phenyl boronic acid (3.6 mmol), Base (9 mmol), Catalyst used (Cu(2wt%)-Pd(4wt%)-Ti, Temperature (90 °C), DMF (10 mL), Time (20 hours), Catalyst amount (0.1 g) action has been carried out at 90 °C and atmospheric pressure condition. Cu-Ti, Pd-Ti and Cu-pd-Ti catalysts with different concentrations were applied for the reaction and maximum yield was obtained for Cu(2wt%)-Pd(4wt%)-Ti system. The results are shown in Table 2. Mechanism of Suzuki coupling reaction is shown in Figure 13.

3.8 Analysis of reaction products

All the separated products were characterized by ^{1}HNMR (400 MHz; CDCl3):
4-methylbiphenyl – The spectrum shows a 3H singlet at $\delta = 2.5$ ppm. Multiplet having δ value around 7.07-7.60 represents 9 aromatic protons.
Biphenyl – Spectrum shows a multiplet having δ value around 7.23-7.59 ppm indicates 10 aromatic hydrogen atoms. FT-IR shows a strong band around 2925-2956 cm^{-1} corresponding to doubly bonded 'CH' stretching vibration and another strong band at 1400-1500 cm^{-1} represents doubly bonded carbon-carbon stretching vibrations.
4-nitrobiphenyl – Spectrum shows multiplet at δ value around 7.30-8.29 ppm corresponding to 9 aromatic hydrogen atoms.

4. Conclusion

Effective, recyclable, and environmentally benign Cu/Pd bimetallic supported on mesoporous TiO_2 was prepared by hydrothermal technique and well characterized by techniques, such as: XRD, TG-DTG, SEM-EDX, and XPS. The prepared catalytic systems were successfully employed for Suzuki coupling reactions. Effective solvent, base, and catalyst were DMF, K_2CO_3, and Cu(2wt%)-Pd(4wt%)-Ti, respectively. The bimetallic catalyst was found to be active up to three cycles without any appreciable loss in its activity. All the products were isolated and purified by column chromatography and characterized by ^{1}HNMR spectroscopy.

Table 8. Recycling studies

No. of cycles	% yield
1	75
2	72
3	70

Reaction conditions: Bromobenzene (3 mmol), Phenyl boronic acid (3.6 mmol), Base (9 mmol), Catalyst used (Cu(2wt%)-Pd(4wt%)-Ti, Temperature (90 °C), DMF (10 mL), Time (20 hours), Catalyst amount (0.1 g)

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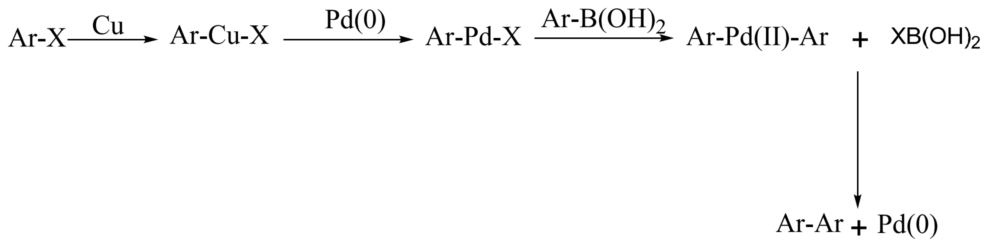

Figure 13. Mechanistic details of Suzuki Coupling reaction

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