

Suzuki-Miyaura Cross-coupling Reaction Catalyzed by Nickel Nanoparticles Supported on Poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ Composite

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Nickel nanoparticle-poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ composite (Ni-PVP/TiO₂-ZrO₂) was prepared by in situ polymerization method. The physical and chemical properties of Ni-PVP/TiO₂-ZrO₂ were investigated by XRD, FT-IR, BET, TGA, SEM and TEM techniques. The catalytic performance of this novel heterogeneous catalyst was determined for the Suzuki-Miyaura cross-coupling reaction between aryl halides and phenylboronic acid in the presence of methanol-water mixture as solvent. The effects of reaction temperature, the amount of catalyst, amount of support, solvent, and amount of metal for the synthesis of Ni-PVP/TiO₂-ZrO₂, were investigated as well as recyclability of the heterogeneous composite. The catalyst used for this synthetically useful transformation showed considerable level of reusability besides very good activity.

Key Words : Poly(*N*-vinyl-2-pyrrolidone), TiO₂-ZrO₂, Ni nanoparticles, Nanocomposite, Polymer-inorganic hybrid material, Suzuki-Miyaura reaction

Introduction

Palladium nanoparticles have become of increasing scientific interest as catalysts for carbon-carbon bond-forming reactions such as Suzuki-Miyaura (SM) cross-coupling reactions, which are among the most useful methodologies in advanced organic synthesis.¹⁻⁴ Usually, carbon-carbon coupling reactions are catalyzed by palladium compound⁵⁻⁷ or Ni-Pd bimetallic catalysts.⁸⁻¹³ On the other hand, the Ni catalysts have many advantages over the Pd catalyst, for example, they are more reactive and often cheaper than the Pd complexes.^{14,15} Ni catalyzed reactions are more specific and are complementary to their Pd analogues. Their air stability, ease of preparation and separation of the catalyst mixture from the product at the end of the reaction sequence are some of the advantages of the Ni catalysts. Ni catalysts have been found to be better catalysts than their Pd counterparts because Ni is smaller in size compared to Pd.^{16,17} Therefore, Ni catalysts have been used for the coupling reactions.¹⁸⁻²³

Most of Suzuki-Miyaura reactions have been carried out in the presence of homogeneous catalysts in the presence of various ligands such as phosphanes, *N*-heterocyclic carbenes, oxime carbapalladacycle, imidazolium, and Schiff's bases.²⁴⁻²⁶ However, the separation and recovery of homogeneous catalysts are not easy, and the resulting products are often contaminated by metal. On the other hand, reusable heterogeneous catalysts are recently attracting much attention due to the increasing international momentum for the development of an environmentally friendly reaction in terms of green chemistry.^{27,28}

Functional polymers are macromolecules to which chemically functional groups are attached; they have the potential

advantages of small molecules with the same functional groups.²⁹ Their usefulness is related both to the functional groups and to their polymeric nature whose characteristic properties mainly depend on the extraordinarily large size of the molecules. The use of polymer-supported reagents provides an attractive and practical method for clean and efficient preparation of novel chemical libraries with potential applications in the pharmaceutical or agrochemical industries.³⁰ Nevertheless, there are relatively a few examples of polymer applications in the field of heterogeneous organocatalysis. It may originate from two drawbacks of most polymers: their low thermal stability, which prevents them from being applied under standard reaction conditions, and/or their low mechanical stability, which prevent their texturing on nanoscale, which is known to be advantageous for catalytic applications.³¹ One way to overcome these drawbacks is the use of organic-inorganic polymer composite instead of polymeric materials.

Hybrid organic-inorganic polymers have been receiving increasing interest from research groups because of their unique properties. These materials combine some of the advantages of polymer compounds (easy processing with conventional techniques, elasticity and organic functionalities) with properties of inorganic oxides (hardness, thermal and chemical stability as well as transparency). Thus, the syntheses of organic-inorganic hybrid polymers with new framework structures are highly desirable.³²⁻³⁵ Nevertheless, among the different researches on these materials, there are relatively a few reports on the application of organic-inorganic hybrid polymer as a heterogeneous catalyst.³⁶⁻³⁹ Recently, in our previous studies,⁴⁰⁻⁴⁴ hybrid organic-inorganic polymers were used as catalysts.

The hybrid materials could be obtained by combining

organic polymers with inorganic materials.⁴⁵ These organic-inorganic hybrid materials could be prepared by various methods, depending on what kind of interaction is employed between organic polymers and inorganic elements, or on how organic moieties are introduced to inorganic phases.

In this research, a novel polymer-inorganic hybrid material, Ni-poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂, was prepared by a simple and inexpensive method without using any bridged organosilanes compound. The catalytic activity of this new polymeric inorganic catalyst was tested for the Suzuki-Miyaura reaction. This catalyst could be reused several times (at least 6) without significant loss of activity/selectivity.

Experimental Method

Catalyst Characterization. The samples were analyzed using FT-IR spectroscopy (using a Perkin Elmer 65 in KBr matrix in the range of 4000-400 cm⁻¹). The BET specific surface areas and BJH pore size distribution of the samples were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Series BEL SORP 18. The X-ray powder diffraction (XRD) of the catalyst was carried out on a Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. Moreover, scanning electron microscope (SEM) studies were performed on Philips, XL30, SE detector. The thermal gravimetric analysis (TGA) data were obtained by a Setaram Labsys TG (STA) in a temperature range of 30-650 °C and heating rate of 10 °C/min in N₂ atmosphere. Transmission electron microscope (TEM) observations were performed on a JEOL JEM.2011 electron microscope at an accelerating voltage of 200.00 KV using EX24093JGT detector in order to obtain information on the size of Ni nanoparticles.

Catalyst Preparation.

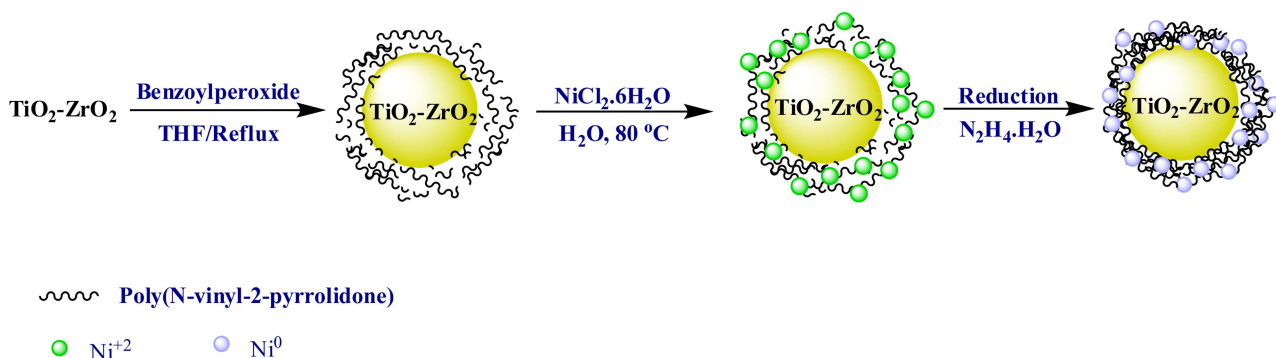
Preparation of TiO₂-ZrO₂ by Sol-gel Method: TiO₂-ZrO₂ was used as support. This support was prepared by the sol-gel method which was described in our previous reports.⁴⁶ In a typical procedure, appropriate amounts of titanium *n*-butoxide and zirconium propoxide were dissolved in the solvent, *n*-butanol to prepare the TiO₂-ZrO₂ catalyst. The solution was heated to 60 °C and the components were thoroughly mixed. Then the solution was cooled down to room temperature, and H-acac as the complexing agent was

added. The mixture was hydrolyzed with deionized water (11.0 mol H₂O/mol alkoxide), containing cetyl pyridinium bromide (CPB) surfactant (mol surfactant/mol alkoxide = 0.1). The solution was left overnight to hydrolyze the alkoxides, yielding transparent gels. The transparent gel was dried at 110 °C to remove water and solvent, and then calcined at 500 °C for 5 h to remove the organics.

Preparation of Poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ (PVP/TiO₂-ZrO₂): *N*-Vinyl-2-pyrrolidone (NVP) (0.5 mL, 4.6 mmol) and TiO₂-ZrO₂ (0.5 g) in 7 mL tetrahydrofuran (THF) were placed in a round bottom flask. Benzoyl peroxide (3 mol %, 0.034 g) was added and the mixture was heated to 65-70 °C for 5 h while being stirred under N₂ gas. The resulting white fine powder composite (PVP/TiO₂-ZrO₂) was collected by filtration, washed several times with THF, and finally dried at 60 °C under reduced pressure.

Preparation of Ni Nanoparticle-poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ (Ni-PVP/TiO₂-ZrO₂): Poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ (PVP/TiO₂-ZrO₂) (0.1 g) and various amounts of aqueous solution of NiCl₂·6H₂O (0.1 M) (1, 2 and 4 mL) with 3 mL of H₂O were placed in a round bottom flask. The mixture was heated for 5 h at 80 °C under N₂ gas. Then, various amounts of aqueous solution of hydrazine hydrates (N₂H₄·H₂O) (80 vol %) (0.15 mL, 0.3 mL and 0.6 mL) was added to the mixture drop by drop in 15-20 minutes. After that, the solution was stirred at 60 °C for 1 h. Afterwards, it was filtered and washed sequentially with chloroform and methanol to remove excess N₂H₄·H₂O and was dried in room temperature to yield Ni nanoparticle-poly(*N*-vinyl-2-pyrrolidone)/TiO₂-ZrO₂ composite (Ni-PVP/TiO₂-ZrO₂) (Scheme 1). The Ni contents of the catalysts were estimated by decomposing the known amount of the catalysts by perchloric acid, nitric acid, fluoric acid, hydrochloric acid, and Ni contents were estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES).

General Procedure for Suzuki-Miyaura Coupling Reaction. In the typical procedure for Suzuki-Miyaura coupling reaction, a mixture of iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (5 mmol), and catalyst (0.14 g, Ni-PVP/TiO₂-ZrO₂) in MeOH/H₂O (3:1, v/v) (5 mL) was placed in a round bottom flask. The suspension was stirred at 60 °C for 8 h. The progress of reaction was monitored by Thin Layer Chromatography (TLC) using *n*-



Scheme 1. Preparation of Ni nanoparticle-PVP/TiO₂-ZrO₂.

hexane as eluent. After completion of the reaction (monitored by TLC), for the reaction work-up, the catalyst was removed from the reaction mixture by filtration, and then the reaction product was extracted with CH_2Cl_2 (3×5 mL). The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired coupling product (97% isolated yield). The product was identified with ^1H NMR, ^{13}C NMR and FT-IR spectroscopy techniques.

Results and Discussion

Catalyst Characterization. Figure 1 depicts the powder X-ray diffraction patterns of the solids $\text{TiO}_2\text{-ZrO}_2$ (a), PVP/ $\text{TiO}_2\text{-ZrO}_2$ (b), Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (c) and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ calcined at 400°C (d). $\text{TiO}_2\text{-ZrO}_2$ showed an amorphous diffraction pattern (Figure 1(a)).⁴⁷ No changes in the diffraction patterns is observed of PVP/ $\text{TiO}_2\text{-ZrO}_2$ (Figure 1(b)), thus reinforcing the assumption that PVP hybridization occurs on the solid surface without changing the structural form of the $\text{TiO}_2\text{-ZrO}_2$. Also, Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ shows an amorphous pattern at 2θ values of $20\text{-}50^\circ$ which doesn't show any peak for nickel. This may occur because the amorphous polymer can be acting as a protective for nickel nanoparticles, so they can't be seen as a distinct peak. In order to prove the existence of the Ni nanoparticles in the composite, the composite was exposed to temperature to remove polymer moieties. The XRD pattern of Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ sample calcined at 400°C can be seen in Figure 1(d). After calcining at 400°C (Figure 1(d)), XRD pattern of nanocomposite showed three characteristic peaks for nickel ($2\theta \sim 44.3, 51.9$ and 76.5) corresponding to the planes (111), (200), and (222).⁴⁸

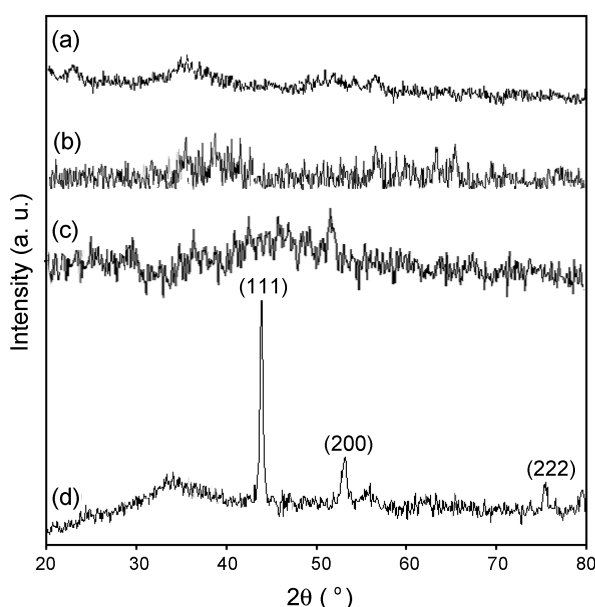


Figure 1. The powder XRD patterns of $\text{TiO}_2\text{-ZrO}_2$ (a), PVP/ $\text{TiO}_2\text{-ZrO}_2$ (b), Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (c) and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ calcined at 400°C (d).

Figure 2 presents the FT-IR spectra of $\text{TiO}_2\text{-ZrO}_2$ (a), PVP/ $\text{TiO}_2\text{-ZrO}_2$ (b), and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (c). In the case of the $\text{TiO}_2\text{-ZrO}_2$ (Figure 2(a)), the broad band in the region $600\text{-}800\text{ cm}^{-1}$ is attributed to Ti-O and Zr-O bonds stretching vibrations.⁴⁹ Moreover, in the FT-IR spectrum of $\text{TiO}_2\text{-ZrO}_2$ (Figure 2(a)) the broad peak around $3400\text{-}3600\text{ cm}^{-1}$ is attributed to the hydroxyl stretching of M-OH and O-H stretching of water, while the peak around 1625 cm^{-1} corresponds to bending mode of O-H of water. These peaks can be seen in the FT-IR spectra of PVP/ $\text{TiO}_2\text{-ZrO}_2$ and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (Figure 2(b), (c)). The existence of PVP in the PVP/ $\text{TiO}_2\text{-ZrO}_2$ composite is evidenced by the appearance of typical PVP vibration on the FT-IR spectrum (Figure 2(b)). In the FT-IR spectrum of PVP/ $\text{TiO}_2\text{-ZrO}_2$ (Figure 2(b)), the new band at 1663 cm^{-1} corresponds to the carbonyl bond of PVP.³⁸ Moreover, the presence of peaks at around $2800\text{-}3000\text{ cm}^{-1}$ corresponds to the aliphatic C-H stretching in PVP/ $\text{TiO}_2\text{-ZrO}_2$ (Figure 2(b)). The appearance of the above bands shows that PVP has been attached to the surface of $\text{TiO}_2\text{-ZrO}_2$ and PVP/ $\text{TiO}_2\text{-ZrO}_2$ has been obtained.

As shown in Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ spectrum (Figure 2(c)), the band around 1663 cm^{-1} which corresponds to carbonyl bond of PVP, is shifted to lower wave numbers (1640 cm^{-1}) (red shift). Moreover, the peak intensity of the carbonyl bond in the spectrum of Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ is lower than that of PVP/ $\text{TiO}_2\text{-ZrO}_2$. This may be due to the interaction between the Ni nanoparticles and C=O groups. This means that the double bond CO stretches become weak by coordinating to Ni nanoparticles. Thus, it is confirmed that PVP molecules exist on the surface of the Ni nanoparticles, and coordinate to the Ni nanoparticles.⁵⁰⁻⁵²

The N_2 adsorption-desorption isotherms of $\text{TiO}_2\text{-ZrO}_2$, PVP/ $\text{TiO}_2\text{-ZrO}_2$ and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ samples are shown in Figure 3, which are similar to the Type IV isotherms

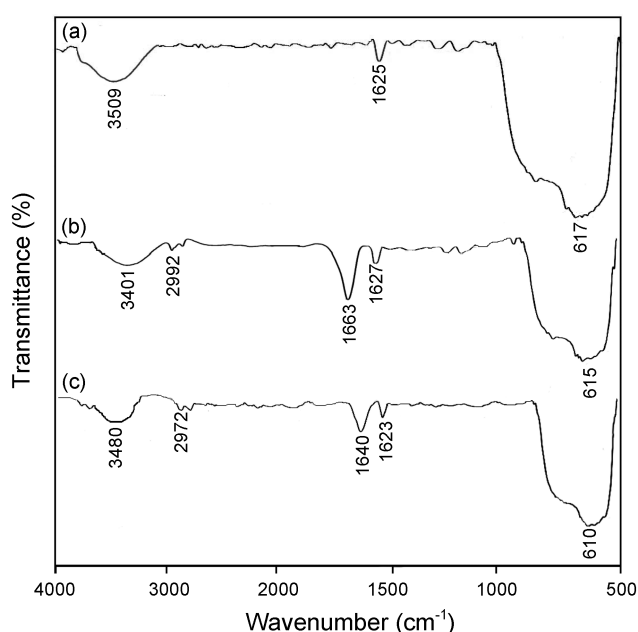


Figure 2. The FT-IR spectra of $\text{TiO}_2\text{-ZrO}_2$ (a), PVP/ $\text{TiO}_2\text{-ZrO}_2$ (b) and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (c).

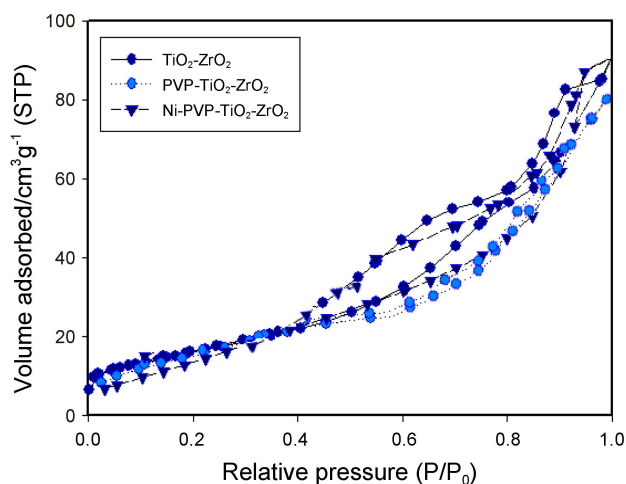


Figure 3. The N_2 adsorption-desorption isotherm of TiO_2 - ZrO_2 , PVP/ TiO_2 - ZrO_2 and Ni-PVP/ TiO_2 - ZrO_2 .

Table 1. Physicochemical properties of TiO_2 - ZrO_2 , PVP/ TiO_2 - ZrO_2 and Ni-PVP/ TiO_2 - ZrO_2 samples obtained from N_2 adsorption

Sample	BET surface area ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$) ^a	Mean pore diameter (nm)
TiO_2 - ZrO_2	83	0.138	9.61
PVP/ TiO_2 - ZrO_2	61	0.104	3.22
Ni-PVP/ TiO_2 - ZrO_2	51	0.105	7.82

^aTotal pore volume.

according to the characteristic of mesoporous materials in IUPAC classification.⁴⁷ From the two branches of adsorption-desorption isotherms, the presence of a sharp adsorption step in the P/P_0 region from 0.4-0.8 and a hysteresis loop at the relative pressure $p/p_0 > 0.7$ shows that the materials possess a well defined array of mesopores. The structure data of all these materials (BET surface area, total pore volume, and pore size) are summarized in Table 1. It is clear that TiO_2 - ZrO_2 has a BET surface area ($83 m^2 g^{-1}$), a pore volume ($0.138 cm^3 g^{-1}$) and a pore size (9.61 nm), indicative of its potential application as a host in organic materials. It is clear that PVP/ TiO_2 - ZrO_2 and Ni-PVP/ TiO_2 - ZrO_2 exhibit a smaller specific surface area in comparison to those of pure TiO_2 - ZrO_2 (61 and $51 m^2 g^{-1}$, respectively) (Table 1). However, there is a noticeable increase in pore diameter for Ni-PVP/ TiO_2 - ZrO_2 , and the pore volume of Ni-PVP/ TiO_2 - ZrO_2 is a little larger than that of PVP/ TiO_2 - ZrO_2 . It might be due to the incorporation of Ni nanoparticles into PVP/ TiO_2 - ZrO_2 . Similar results were reported for such metal incorporation in mesoporous materials.^{53,54} Although there are decreases in the surface area, Ni-PVP/ TiO_2 - ZrO_2 pores were not blocked by deposition of polymers and Ni nanoparticles (Table 1).

Figure 4 presents the TGA curves of TiO_2 - ZrO_2 (a), PVP (b), PVP/ TiO_2 - ZrO_2 (c) and Ni-PVP/ TiO_2 - ZrO_2 (d) under N_2 atmosphere. The mass loss at temperature $< 100 ^\circ C$ (around 6%, w/w) is attributed to desorption of water present in the surfaces of TiO_2 - ZrO_2 (Figure 4(a)). The TGA curve of PVP shows a small mass loss (around 7.5%, w/w) in the temper-

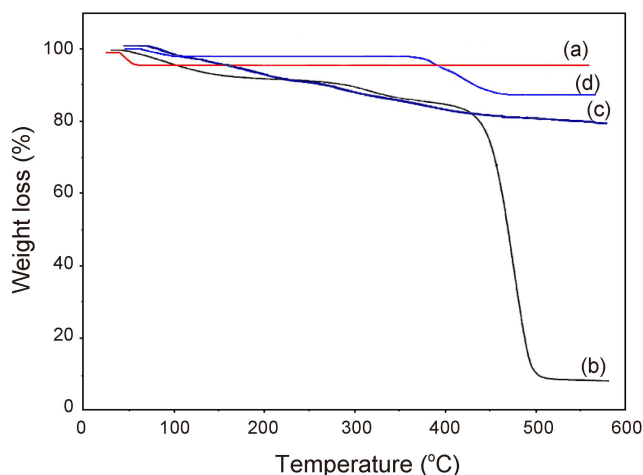


Figure 4. TGA curves of TiO_2 - ZrO_2 (a), PVP (b), PVP/ TiO_2 - ZrO_2 (c) and Ni-PVP/ TiO_2 - ZrO_2 (d).

ature range 50 - $150 ^\circ C$, which is apparently associated with adsorbed water (Figure 4(b)). At temperatures above $200 ^\circ C$, PVP shows one main stage of degradation. The mass loss for PVP in the second step is equal to 77% (w/w) which corresponds to the effective degradation of the polymer (Figure 4(b)). Thermo analysis of PVP/ TiO_2 - ZrO_2 shows two steps of mass loss (Figure 4(c)). The first step (around 3%, w/w) that occurs in the temperature range 50 - $150 ^\circ C$, is related to desorption of water. The second step (around 13%, w/w) which started at $200 ^\circ C$ is attributed to the degradation of the polymer, and the degradation ended at $550 ^\circ C$ (Figure 4(c)). By comparing the PVP and PVP/ TiO_2 - ZrO_2 curves, one can find that PVP/ TiO_2 - ZrO_2 shows a slower degradation rate than PVP (Figure 4(b), (c)). Therefore, after hybridization, the thermal stability is enhanced greatly, and this is very important for the catalyst application. However, for Ni-PVP/ TiO_2 - ZrO_2 sample, two separate weight loss steps are seen (Figure 4(d)). The first step (around 2%, w/w) appearing at temperature $< 100 ^\circ C$ corresponds to the loss of water. The second weight loss (about 350 - $450 ^\circ C$) amounting to around 9% (w/w) is related to the degradation of the polymer. Obviously, Ni-PVP/ TiO_2 - ZrO_2 has higher thermal stability than PVP/ TiO_2 - ZrO_2 , which may be attributed to the presence of Ni nanoparticles in the composite structure. Therefore, it is very important for the catalyst application that the thermal stability be enhanced greatly after hybridization.

Figure 5 gives the scanning electron microscopy (SEM) photographs of TiO_2 - ZrO_2 (a) and Ni-PVP/ TiO_2 - ZrO_2 (b) samples. Virtually, the difference in particle surface morphology between the TiO_2 - ZrO_2 and Ni-PVP/ TiO_2 - ZrO_2 composite indicates that polymers and Ni nanoparticles are distributed on the surfaces of TiO_2 - ZrO_2 .

The TEM micrograph of Ni-PVP/ TiO_2 - ZrO_2 was depicted in Figure 6. The places with darker contrast could be assigned to the presence of Ni nanoparticles with different dispersion. This assumption was confirmed by EDX data. It can be seen from Figure 6 that spherically shaped Ni nanoparticles (average diameter of ~ 3 - 5 nm) were formed.

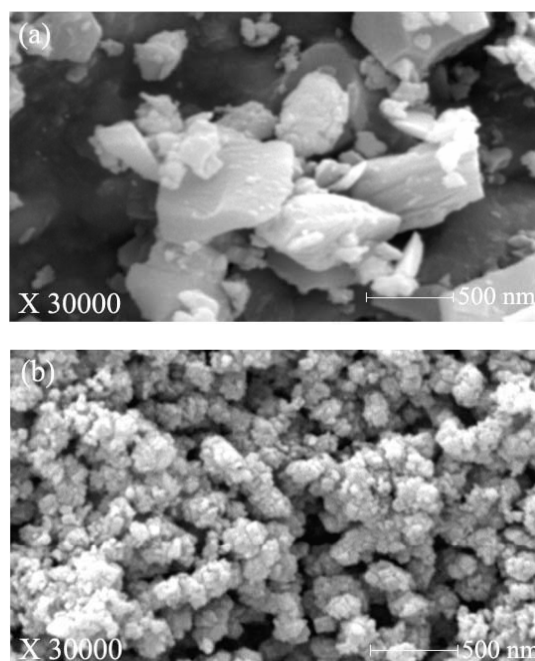


Figure 5. SEM figures of $\text{TiO}_2\text{-ZrO}_2$ (a) and $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ (b).

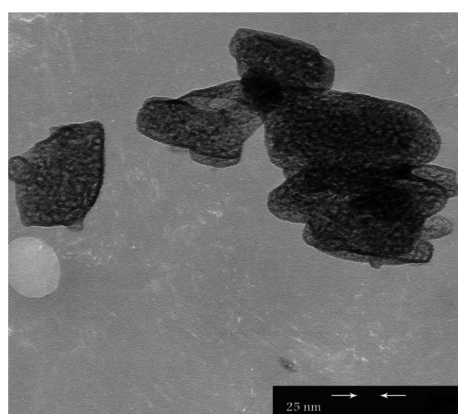


Figure 6. TEM image of $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$.

Catalytic Activity. $\text{Ni-PVP/ZrO}_2\text{-TiO}_2$ nanocomposite was used as a catalyst for Suzuki-Miyaura reactions of various aryl halides with phenylboronic acid.

To optimize the reaction conditions, a model reaction was carried out by taking iodobenzene and phenylboronic acid in different solvents and bases at 60 °C. Solvent plays a crucial role in the rate and the product distribution of Suzuki-Miyaura reactions. In this context, different solvents were used: H_2O , $\text{MeOH/H}_2\text{O}$ (3:1, v/v), CH_3CN , MeOH or dioxane, and the reaction was catalyzed with 0.14 g of $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ catalyst in the presence of 5 equivalents of base and with an iodobenzene/phenylboronic acid ratio of 1 to 1.5 (Table 2). According to the results presented in Table 2, $\text{MeOH/H}_2\text{O}$ (3:1, v/v) was selected as the solvent for the reaction because it is highly efficient, less expensive, and readily available.

The reaction was also carried out at different temperatures in $\text{MeOH/H}_2\text{O}$ (3:1, v/v). The reaction was performed at

Table 2. Effect of solvent on Suzuki-Miyaura reaction^a

Solvent	Yield (%) ^b
H_2O	20
MeOH	40
$\text{MeOH:H}_2\text{O}$ (3:1 v/v)	97
CH_3CN	50
Dioxane	60

^aReaction conditions: $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), solvent (5 mL), 60 °C, 8 h. ^bIsolated yield.

Table 3. Effect of different temperature on Suzuki-Miyaura reaction^a

Temperature (°C)	Yield (%) ^b
25	60
40	82
60	97

^aReaction conditions: $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), $\text{MeOH/H}_2\text{O}$ (3:1 v/v) (5 mL), 8 h. ^bIsolated yield.

Table 4. Effect of different base on Suzuki-Miyaura reaction^a

Base	Yield (%) ^b
K_2CO_3	97
Na_3PO_4	44
Na_2CO_3	61
Et_3N	33

^aReaction conditions: $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), base (5 mmol), $\text{MeOH/H}_2\text{O}$ (3:1, v/v) (5 mL), 60 °C, 8 h. ^bIsolated yield.

25 °C, 40 °C and 60 °C. The results are presented in Table 3. The yield was increased from 60% to 97% by increasing the temperature from 25 °C to 60 °C. At room temperature, low amount of coupled product was obtained. Increasing the temperature from 25 to 60 °C improved the conversion (Table 4, entries 1-3), while with further increase in temperature, no such improvement in the conversion was obtained.

The effect of base on the coupling reaction was evaluated by taking iodobenzene (1 mmol) with phenylboronic acid (1.5 mmol) in $\text{MeOH/H}_2\text{O}$ (3:1, v/v) at 60 °C in the presence of $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ (0.14 g) with various bases (5 mmol) (Table 4). Various bases such as Na_2CO_3 , K_2CO_3 , Et_3N , and Na_3PO_4 were examined for the reaction. The results revealed that the inorganic bases used were more effective than organic bases like Et_3N (Table 5) and hence the economically cheaper K_2CO_3 was chosen as a base for these coupling reactions.

In order to investigate the effect of $\text{TiO}_2\text{-ZrO}_2$ on catalytic activity, different kinds of $\text{Ni-PVP/TiO}_2\text{-ZrO}_2$ catalysts in which the amount of the $\text{TiO}_2\text{-ZrO}_2$ were 0.0, 0.25, 0.5 and 1 g, for polymerization of 0.5 mL NVP, were prepared and used in Suzuki-Miyaura reaction. Table 5 displays the experimental results. The best result was obtained when ratio of $\text{TiO}_2\text{-ZrO}_2$ (g) to NVP (mL) was 1:1. Obviously, the

Table 5. Effect of $\text{TiO}_2\text{-ZrO}_2$ amount on catalytic activity of composite Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ ^a

Entry	Amount of NVP/ $\text{TiO}_2\text{-ZrO}_2$ (mL/g)	Yield (%) ^b
1	0.5/0	37
2	0.5/0.25	54
3	0.5/0.5	97
4	0.5/1	67

^aReaction conditions: Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), MeOH/ H_2O (3:1, v/v) (5 mL), 60 °C, 8 h. ^bIsolated yield.

greater amount of $\text{TiO}_2\text{-ZrO}_2$ did not lead to the higher catalytic activity of the Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ as a catalyst, because the amounts of active species of catalyst (Ni-PVP) decreased. In addition, when the amounts of $\text{TiO}_2\text{-ZrO}_2$ were decreased in the composite (NVP (mL) to $\text{TiO}_2\text{-ZrO}_2$ (g) ratio was 0.5 (mL): 0.25 (g)), the catalytic activity of the catalyst was decreased. One of the greatest advantages of this catalyst was to easily use due to its powdery structure. Ni-PVP was adhesive and this character made it hard to separate it from the vessel; but after mixing with $\text{TiO}_2\text{-ZrO}_2$ and making Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ composite, it becomes powdery which was easily to be used and recycled. Therefore, by decreasing the amount of $\text{TiO}_2\text{-ZrO}_2$ in the composite, the composite was adhesive and the catalytic activity was decreased.

Also comparative reaction by using Ni-PVP and Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ showed that Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ was more efficient, by completion the reaction in a short time. On the other hand, the yield was decreased and the reaction was carried out in a long period of time using Ni-PVP. It was obvious that composite Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ systems (entry 2, 3, 4) were advantageous. In fact, the activity of Ni-PVP was much lower than those of Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ with various ratios of polymer to $\text{TiO}_2\text{-ZrO}_2$ (entry 2, 3, 4). It should be noticed that when $\text{TiO}_2\text{-ZrO}_2$ used as a catalyst, the reaction did not proceed significantly.

The effect of the amount of the catalyst was determined for Suzuki-Miyaura reaction. It can be seen that with an increase in the amount of catalyst from 0.06 g to 0.14 g, a considerable increase in the yield was observed from 40% to 97% (Table 6). Thus, the quantity of 0.14 g was found to be the best weight of composite for the condensation of iodobenzene (1 mmol) with phenylboronic acid (1.5 mmol) in MeOH/ H_2O (3:1, v/v) (5 mL) at 60 °C. In addition, it could be seen that in the absence of the catalyst, there weren't any products.

To identify the effect of nickel nanoparticle concentration on the Suzuki-Miyaura reaction, different amounts of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ were examined (Table 7). The amounts of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ were changed from 0.1 mmol to 0.4 mmol while the other values were constant (the molar ratio of NiCl_2 to $\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$ was 1:23). As shown in Table 7, the catalytic activity was improved by increasing the amount of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$. When the amount of nickel increased from 0.1 mmol to 0.2 mmol the yield increased from 90% to 97%.

Table 6. Effect of catalyst amount on Suzuki-Miyaura reaction^a

Amount of catalyst (g)	Yield (%) ^b
0	-
0.06	40
0.08	61
0.10	69
0.12	89
0.14	97

^aReaction conditions: Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$, iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), MeOH/ H_2O (3:1, v/v) (5 mL), 60 °C, 8 h. ^bIsolated yield.

Table 7. Effect of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ amount on catalytic activity of composite Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ ^a

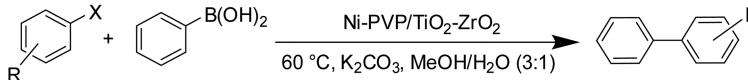
Amount of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (mmol)	Yield (%) ^b	Ni content of catalyst (mmol g ⁻¹) ^c
0.1	90	0.936
0.2	97	1.74
0.4	97	1.83

^aReaction conditions: Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), MeOH/ H_2O (3:1, v/v) (5 mL), 60 °C, 8 h. ^bIsolated yield. ^cEstimated by ICP-AES technique.

By increasing nickel chloride concentration, the amount of active sites (Ni nanoparticles) on the catalyst increased. Therefore, higher nickel chloride concentrations showed a better catalytic activity. However, with further increase in the amount of nickel chloride, the nickel content of the catalyst didn't change significantly, so the catalytic activity of the catalyst didn't changed. It should be mentioned that, when $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ used homogeneously as a catalyst, the yield of the reaction was only 13% after 24 h.

Suzuki-Miyaura reactions of different aryl halides and phenylboronic acid with 0.14 g of Ni-PVP/ $\text{TiO}_2\text{-ZrO}_2$ as catalyst were investigated. Reactions were carried out in MeOH/ H_2O (3:1, v/v) at 60 °C and different times. The results are listed in Table 8. It is well known that activation of C-Br bond is much more difficult than C-I bonds, and in general requires harsher reaction conditions in heterogeneous catalysis system.⁵⁵⁻⁵⁸ However, aryl bromides afforded excellent coupling products (entry 4, 6, 7) but needed more time than that of aryl iodides. Aryl iodides (entries 1, 2, 3, 5) afforded excellent coupling products. Thus, the catalyst afforded excellent yields of the biaryl products at 60 °C.

Reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst in the case of the model reaction (Table 9). After each cycle, the catalyst was filtered off, washed with water (10 mL), diethyl ether and acetone (3 × 5 mL). Then, it was dried in oven at 60 °C and reused in the Suzuki-Miyaura reaction. The results showed that this catalyst could be reused without any modification, 6 times and no significant loss of activity/selectivity performance was observed. It should be mentioned that there was very low Ni leaching during the reaction and the catalyst exhibited high stability even after 6 recycles (Table 9). The Ni content of the

Table 8. Suzuki-Miyaura reaction of aromatic aryl halides and phenylboronic acid catalyzed by Ni-PVP/TiO₂-ZrO₂^a


Entry	Substrate	Product	Yield (%) ^b	Time (h)	mp (°C)	
					Found	Reported ^{ref}
1			97	8	71-73	70-72 ⁵⁹
2			97	10	47-49	45-50 ⁵⁹
3			95	10	53-55	55-56 ⁶⁰
4			98	14	121-123	120-122 ⁵⁹
5			95	10	31-35	32.5-33.5 ⁵⁹
6			97	12	71-73	70-72 ⁵⁹
7			95	12	71-73	70-72 ⁵⁹
8			63	24	71-73	70-72 ⁵⁹

^aReaction conditions: Ni-PVP/TiO₂-ZrO₂ (0.14 g), aryl halide (1 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (5 mmol), MeOH/H₂O (3:1, v/v) (5 mL), 60 °C. ^bIsolated yield.

Table 9. The catalyst reusability for Suzuki-Miyaura reaction^a

Cycle	Yield (%) ^b	Ni content of catalyst (mmol g ⁻¹) ^c
fresh	97	1.74
1	97	1.74
2	97	1.74
3	97	1.71
4	96	1.69
5	96	1.69
6	95	1.69

^aReaction conditions: Ni-PVP/TiO₂-ZrO₂ (0.14 g), iodobenzene (1 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (5 mmol), MeOH/H₂O (3:1, v/v) (5 mL), 60 °C, 8 h. ^bIsolated yield. ^cEstimated by ICP-AES technique.

used catalyst (after 6 cycles) determined by ICP-AES was 1.69 mmol g⁻¹ which was about only 3% lower than the fresh catalyst (Table 9).

The commonly accepted mechanism for the Suzuki reaction involves the initial oxidative addition of the aryl halide to a zero-valent metal species, followed by trans metalation and reductive elimination to give the coupling product and restore the catalytically active nickel(0) species (Scheme 2). In this condition, nickel(0) is regenerated, which then deposits back on to the surface of the support (re-deposition).

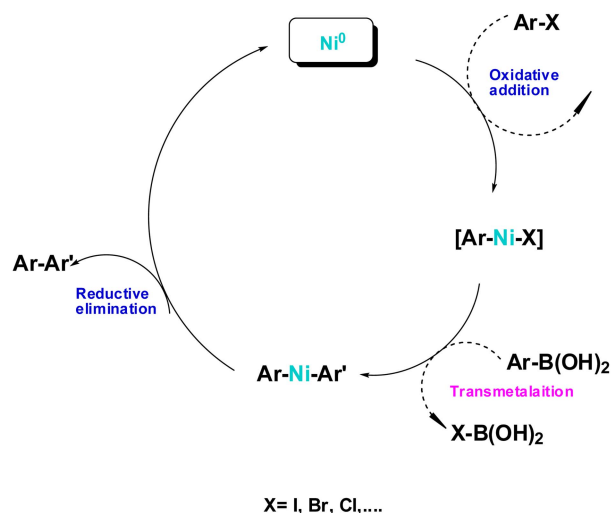
**Scheme 2.** Proposed mechanism for Suzuki-Miyaura cross-coupling reaction catalyzed by Ni-PVP/TiO₂-ZrO₂.

Table 10 shows the comparison between the catalyst used in the present study and other Ni catalysts reported in the literature for SM reaction.¹⁸⁻²³ As can be seen, Ni-PVP/TiO₂-ZrO₂ catalyst shows good activity and reasonable yield for SM reaction of aryl halides and phenylboronic acid in a

Table 10. Comparison of catalytic activity of Ni-PVP/TiO₂-ZrO₂ with other Ni catalysts

Catalyst	Substrate	Product	Solvent	Temperature (°C)	Yield (%)	Time (h)	Ref.
Ni nanoparticles	4-bromoacetophenone	4-acetylbiphenyl	DMSO	135	98	-	18
Ni(0)/TBAB	iodobenzene	biphenyl	EtOH	80	98	6	19
Ni(COD) ₂ /Ligand	4-methylchlorobenzene	biphenyl	THF	R.T	99	48	20
Ni(COD) ₂ /Ligand chloronickel tetraauroborate complex	4-methylchlorobenzene	biphenyl	THF	reflux	60	24	21
	4-bromoacetophenone	4-acetylbiphenyl	BuOH	120	83	2	22
Ni(0) powder	iodobenzene	biphenyl	PEG-400	110 under N ₂	91	10	23
Ni-PVP/TiO ₂ -ZrO ₂	iodobenzene	biphenyl	MeOH/H ₂ O	60	98	8	This work
Ni-PVP/TiO ₂ -ZrO ₂	4-bromoacetophenone	biphenyl	MeOH/H ₂ O	60	98	14	This work
Ni-PVP/TiO ₂ -ZrO ₂	chlorobenzene	biphenyl	MeOH/H ₂ O	60	63	24	This work

reasonable time with high yields in the presence of a green solvent. In addition, the reusability of Ni-PVP/TiO₂-ZrO₂ was considerable.

Conclusion

A novel polymer-inorganic hybrid material (Ni-PVP/TiO₂-ZrO₂) is prepared by a simple and inexpensive method without using any expensive Pd compounds. This new solid catalyst become practical alternatives to homogenous catalysts in view of the following advantages: a) high catalyst activity under mild reaction conditions; b) easy separation of the catalyst after the reaction; c) reusability of the catalyst for several times without any loss in yield of the reaction. Finally, we believe that the new synthetic method reported here would greatly contribute to a process which is safe for the environmentally.

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