Palladium Supported on Zinc Oxide Nanoparticles as Efficient Heterogeneous Catalyst for *Suzuki–Miyaura* and *Hiyama* Reactions under Normal Laboratory Conditions

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Nanoscale Pd supported on ZnO was prepared by a facile coprecipitation method. Pd/ZnO Nanoparticles were characterized by using XRD, TEM, SEM, XPS, *BET* specific surface area measurement, and thermogravimetric analysis. This catalyst was used as novel and excellent heterogeneous catalyst for ligand-free C–C bond-formation particularly in the synthesis of unsymmetrical biaryls by *Suzuki–Miyaura* and *Hiyama* cross-coupling reactions under air atmosphere without use of any Ar or N_2 flow. The catalyst can be recovered and recycled several times without marked loss of activity.

Introduction. – Pd Catalysts are used in C–C coupling reactions including *Suzuki–Miyaura* and *Hiyama* cross coupling [1]. Despite its remarkable usefulness, homogeneous Pd catalysts suffer from a number of drawbacks such as availability, stability, costs of the Pd complexes and phosphine ligands, and they are not used in industrial applications because of difficult separation and recycling procedure [2]. Therefore, heterogeneous Pd catalysts have been developed and seem particularly well suited since the Pd metal immobilized onto a support (including organic, polymeric, or inorganic support materials) could be easily removed by filtration leaving products virtually free of residual Pd [1][3]. Pd Nanoparticles and colloidal Pd species have also been reported as recyclable catalysts [4][5]. However, these heterogeneous Pd catalysts often suffer from problems, such as low catalytic efficiency, degradation, leaching of the metal species, and difficult synthetic procedures.

Among the important II–VI semiconductors, ZnO has been widely studied because of its fundamental properties and potential uses in devices, such as gas sensors, solar cells, resonators, field-effect transistors, and catalyst [6]. In recent years, the modification of ZnO with noble metals, such as Ag, Au, Pt, and Pd, has attracted significant attention [7]. As a noble metal, Pd, whose ionic radius (0.080 nm) is close to that of Zn^{2+} (0.074 nm), has been widely used in industrial catalysis especially for MeOH synthesis [8]. However, modifying ZnO with Pd has already been applied in the area of catalytic reaction [8][9]; to the best of our knowledge, there are a few studies on C–C coupling reactions with ZnO modified with Pd [10][11]. *Kim* and *Choi* [10] reported a method for preparing Pd/ZnO and Pd–M (M = Cu, Ni, and Ag) nanoparticles (Pd–M/ZnO) by γ-irradiation and their catalytic efficiencies were evaluated in hydrogenation and *Suzuki* reactions. But, these systems actually suffer from huge drawbacks, such as using large amounts of ZnO nanopowder, N_2 gas to remove O_2 from

the reaction vessel, γ-ray irradiation, and organic solvents, such as MeOH, or in the case of *Suzuki* C–C coupling reactions the limitation to only iodohalides and phenylboronic acid and the use of EtOH as solvent. Also, the molar ratio of iodohalide/ phenylboronic acid/Pd/ZnO catalyst was $1:2:1.3$, and the loaded amount of Pd on ZnO, which was determined by ICP data, was 19.4 wt%. Up to now, other supported Pd catalysts have been reported for *Suzuki* reactions of aryl halides under different reaction conditions [12]. Though, there are still problems, such as long reaction times, using organic solvents, or using ligands [12f].

In the present study, we focused on the preparation of Pd/ZnO, which appeared to be one of the best catalysts for *Suzuki–Miyaura* and *Hiyama* reactions. The aim of our work described in this article was the synthesis of Pd supported on ZnO by coprecipitation (CP) method (Pd loading was 9.84 wt%, determined by ICP) for ligand-free C–C bond-formation by *Suzuki* and *Hiyama* reactions in H_2O and ethyleneglycol, respectively.

Results and Discussion. – As part of our continuing attempts to broaden the scope of nano metal oxides as catalysts [10][12a][12c], we have recently reported the efficiency of nano Pd/ZnO in *Mizoroki–Heck* and *Sonogashira* reactions, and also for the formation of C–O and C–N bonds [13]. This catalyst was synthesized and fully characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), *BET* surface area measurement, FT-IR spectroscopy, inductively coupled plasma (ICP) analysis, and atomic absorption spectroscopy (AAS) analysis, some of these results are shown in *Table 1*, and *Figs. 1 – 5* [13]. SEM and TEM images of the synthesized Pd/ZnO nanoparticles are shown in *Fig. 1*. The amount of Pd supported on ZnO nanoparticles was determined by ICP technique. According to this analysis, the amounts of Pd in 0.001 and 0.009 g of the catalyst were determined as $925 \cdot 10^{-9}$ and $8325 \cdot 10^{-9}$ mol-%, respectively.

The activity of Pd/ZnO nanoparticle catalyst was first examined in the *Suzuki–Miyaura* reaction. This choice was based on the fact that such a reaction provides a powerful tool for C–C coupling for the synthesis of many natural and synthetic biaryls. To determine the optimal reaction conditions, the cross coupling of 1-(4-bromophenyl)ethanone (1 mmol) in the presence of Pd/ZnO nanoparticles was studied under variation of different parameters, such as solvent, base, temperature, and amount of catalyst (*Scheme* and *Tables 2 – 5*).

Table 1. *Physical Characterization of Nano Pd/ZnO*

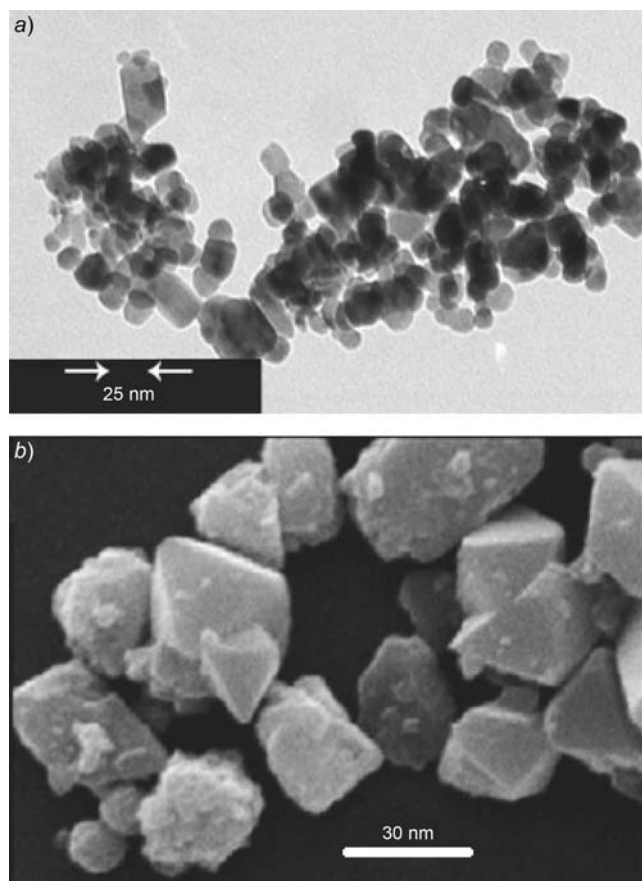|	
XRD	Crystallite sizes of ZnO and Pd/ZnO: 21 – 23 nm
BET Surface area	$40.61\ m^2\,g^{-1}$
Pore size distribution	1.81 nm
TEM	25 nm
XPS	Binding energy of the $Pd_{3d5/2}$: 335.5 eV
TGA	Percentage of accessible Pd in catalyst: $2.72 \pm 0.01\%$
ICP	9.84%
AAS	9.80%

Fig. 1. a) *TEM and* b) *SEM images of nano Pd/ZnO*

At first, the base was optimized (*Table 2*). Various bases were tested and all of them gave similar results. As can be seen from *Entry 8*, this reaction can occur even without any addition of base, but the reaction time increased and the yield of the product decreased. Compared with *Entries 5 – 7*, with addition of 0.25 mmol K_2CO_3 the yield of the product was much better, therefore, K_2CO_3 as an inexpensive and readily available inorganic base was used in this study.

As the results listed in *Table 3* revealed that the selection of solvent was also important for the presented method. Using H_2O as solvent gave satisfactory results, whereas the use of other protic and aprotic polar solvents, such as EtOH, ethane-1,2-diol, DMSO, and DMF, which are commonly used in Pd-catalyzed coupling reactions, was not very effective. Thereafter, we examined the effect of temperature. The results are shown in *Table 4*. Finally, the amounts of Pd/ZnO nanoparticles were optimized (*Table 5*). As it can be seen from *Entries 2 – 4*, by increasing the amount of catalyst from 0.0005 g to 0.005 g, the yield of the desired product was not changed, but the reaction time decreased. A catalytic amount of 0.001 g (which contains $925 \cdot 10^{-9}$ mol-% Pd;
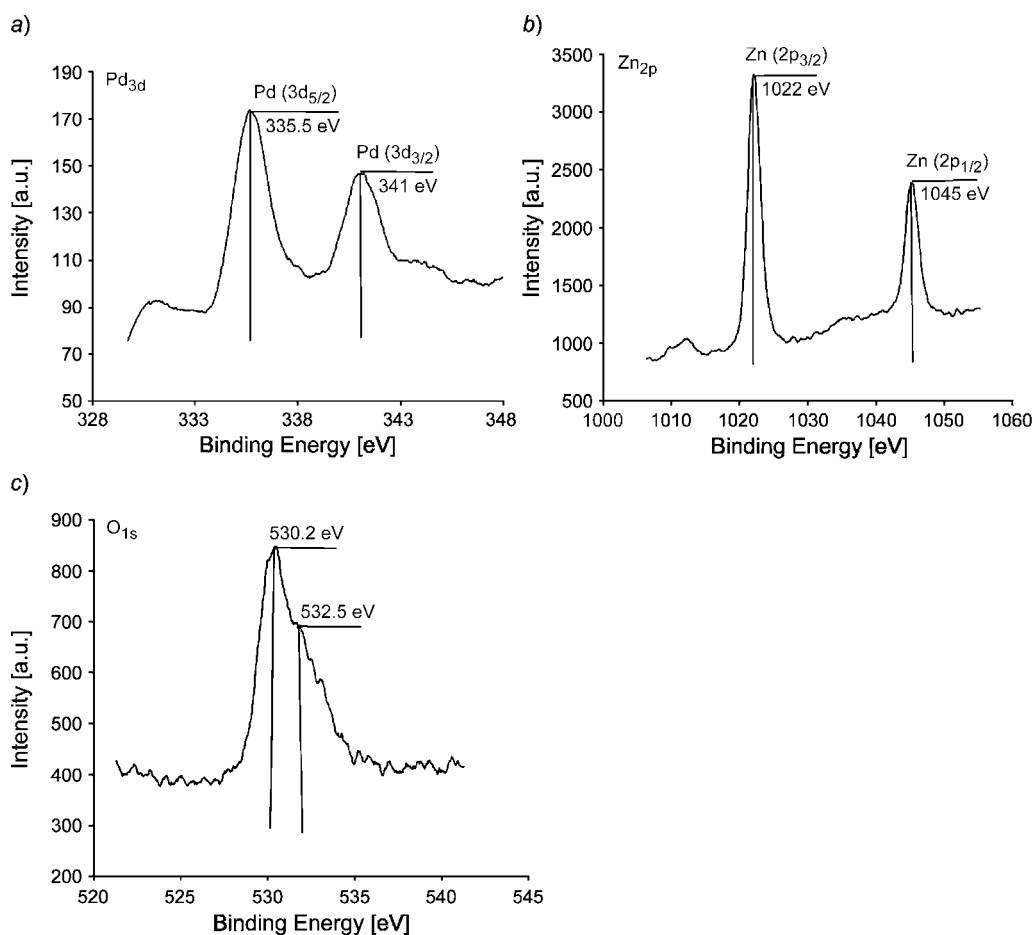
Fig. 2. *XPS Spectra of* a) *Pd$_{3d}$,* b) *Zn$_{2p}$, and* c) *O$_{1s}$ of 9.8 wt% nano Pd/ZnO*

Entry 3) was applied because of the lower amount of Pd loading compared with 0.005 g (*Entry 4*). Also, nano ZnO was prepared without modification with Pd by the same procedure as for the preparation of Pd/ZnO. As expected, no reaction occurred with nano ZnO (*Table 5, Entry 5*).

On the basis of the optimized reaction conditions, coupling reactions between aryl halides (X = I, Br, and Cl) and different arylboronic acids were carried out. The results are shown in *Table 6*. The reaction of aryl iodides, bromides, and chlorides with a variety of electron-rich and electron-poor substituents proceeded smoothly, giving the coupling products in good to excellent yields. In addition, various arylboronic acids with electron-donating or electron-withdrawing substituents were also used in this reaction (*Table 6*). It was found that the yields of the coupling reactions decreased slightly for arylboronic acids containing electron-withdrawing groups, such as (3,4,5-trifluorophenyl)boronic acid, while the reactions with arylboronic acids with electron-rich groups, such as (4-ethylphenyl)boronic acid, proceeded more efficiently than those
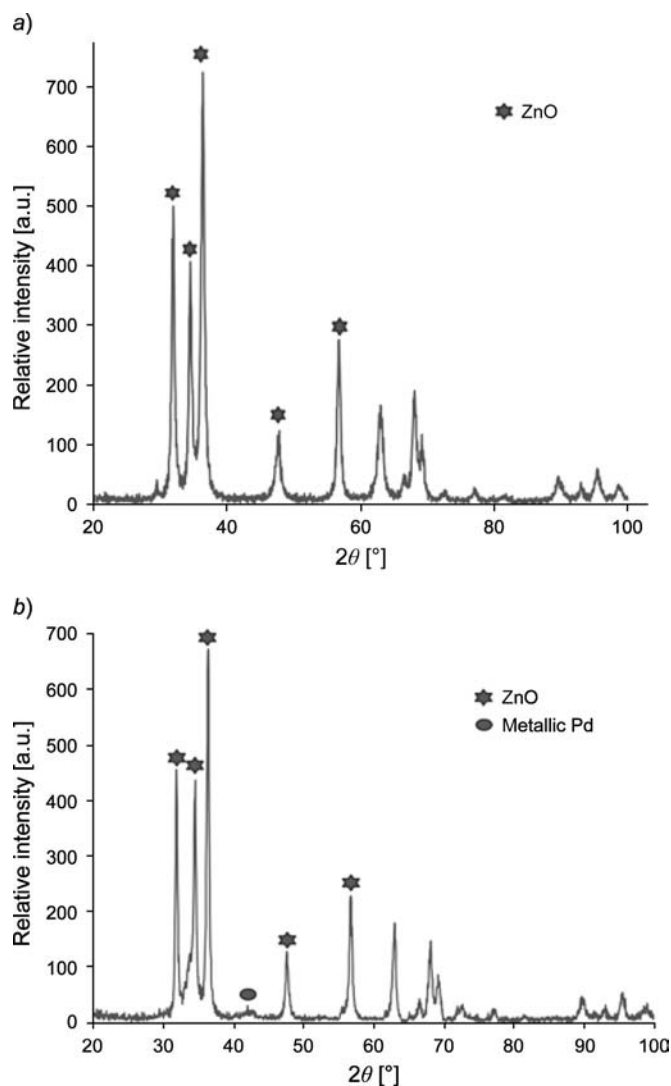
Fig. 3. *XRD Pattern of* a) *nano ZnO and* b) *9.84 wt% of Pd-modified ZnO calcined at 723 K for 2 h*

of phenylboronic acid in agreement with the results reported by *Liu* and co-workers [14]. This is due to the effect of the substituents on the nucleophilicity of arylboronic acids. The stronger the nucleophilicity, the more active is the arylboronic acid. Furthermore, steric hindrance due to *ortho*-substituents on the aryl iodides affected the reaction progress. Thus, the reaction time for 1-iodo-2-methylbenzene was higher than for 4-substitued iodobenzenes (*Table 6*, *Entries 5* and *6*). Because some of the NO_2 and CN substrates were insoluble and solid in H_2O at 100°, a mixture of H_2O/EtOH 1:1 under reflux, in which the substrates were soluble, was used as solvent (*Table 6*, *Entries 4*, *11*, and *16*).
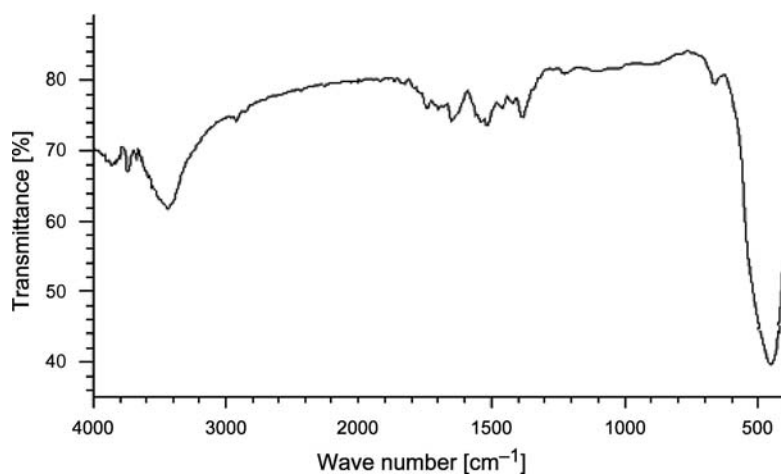
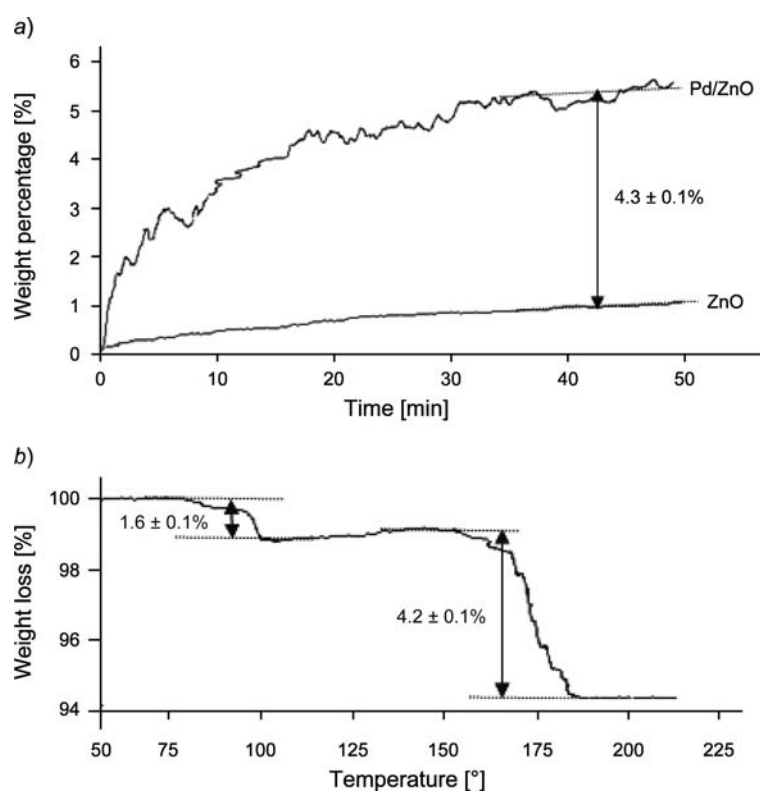Fig. 4. *FT-IR Spectrum of nano Pd/ZnO*

Fig. 5. a) *Trace showing the interaction of CO as molecular probe with ZnO and Pd/ZnO nanoparticles.*
b) *Thermogram showing the interaction of CO as molecular probe with Pd/ZnO nanoparticles under N_2 atmosphere.*

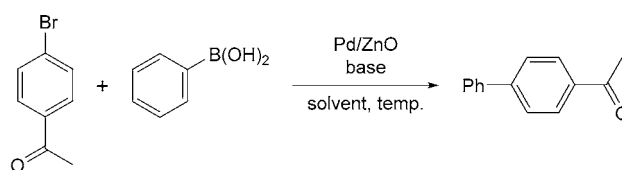Scheme. *Suzuki Reaction of 1-(4-Bromophenyl)ethanone and Phenylboronic Acid Using Pd/ZnO Nanoparticles as Catalyst*

Table 2. *Optimization of Bases*[a])

Entry	Base	Amount of base [mmol]	Time [h]	Yield[b]) [%]
1	Na$_2$CO$_3$	1	1	96
2	KF·2 H$_2$O	1	1	96
3	K$_3$PO$_4$	1	0.5	96
4	KOH	1	1	96
5	K$_2$CO$_3$	1	0.25	96
6	K$_2$CO$_3$	0.5	0.5	96
7	K$_2$CO$_3$	0.25	0.5	96
8	None	–	3	80

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), phenylboronic acid (1 mmol), Pd/ZnO nanoparticles (0.001 g), H$_2$O (1 ml), and base, 100°. [b]) Yield of isolated product.

Table 3. *Optimization of Solvents*[a])

Entry	Solvent	Time [h]	Yield[c]) [%]
1	H$_2$O	0.5	96
2	EtOH	0.75	90
3	H$_2$O/EtOH 1:1	0.70	95
4	Ethane-1,2-diol	6	15
5	Toluene	6	20
6[b])	CH$_2$Cl$_2$	6	15
7	DMSO	6	60
8	DMF	6	70
9	None	6	60

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), phenylboronic acid (1 mmol), Pd/ZnO nanoparticles (0.001 g), H$_2$O (1 ml), K$_2$CO$_3$ (0.25 mmol), and solvent (1 ml), 100°. [b]) Reaction conducted at 50°. [c]) Yield of isolated product.

Table 4. *Optimization of Temperatures*[a])

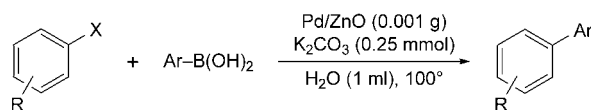| Temperature [°]	100	80	70	60	50	r.t.
Time [h]	0.5	0.75	2	5	10	24
Yield [%][b])	96	96	96	90	80	70

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), phenylboronic acid (1 mmol), Pd/ZnO nanoparticles (0.001 g), H$_2$O (1 ml), K$_2$CO$_3$ (0.25 mmol). [b]) Yield of isolated product.

Table 5. *Optimization of the Amounts of Pd/ZnO Nanoparticles*[a])

Entry	Pd/ZnO [g] ([mol-% of Pd][b])[c])	Time [h]	Yiel[d]) [%]
1	0.0001 ($925 \cdot 10^{-10}$)	4	95
2	0.0005 ($4625 \cdot 10^{-10}$)	2	96
3	0.001 ($925 \cdot 10^{-9}$)	0.5	96
4	0.005 ($4625 \cdot 10^{-9}$)	0.25	96
5[c])	0.001	24	None

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), phenylboronic acid (1 mmol), H_2O (1 ml), K_2CO_3 (1 mmol), and Pd/ZnO nanoparticles, 100°. [b]) Determined by ICP. [c]) Nano ZnO as catalyst. [d]) Yield of isolated product.

Table 6. Suzuki–Miyaura *Reaction of Aryl Halides with Arylboronic Acids Catalyzed by Pd/ZnO Nanoparticles*

Entry	X	R	Ar	Time [min]	Yield[b]) [%]
1	I	H	Ph	50	96
2	I	4-MeO	Ph	60	84
3	I	4-NH$_2$	Ph	90	93
4[a])	I	4-NO$_2$	Ph	45	96
5	I	2-Me	Ph	120	90
6	I	4-Me	Ph	90	94
7	Br	H	Ph	240	90
8	Br	4-Me	Ph	300	92
9	Br	4-MeO	Ph	360	89
10	Br	4-OH	Ph	25	90
11[a])	Br	4-CN	Ph	40	94
12	Br	4-Ac	Ph	30	96
13	Cl	H	Ph	300	89
14	Cl	4-Me	Ph	360	87
15	Cl	4-CN	Ph	55	92
16[a])	I	4-NO$_2$	3,4,5-F$_3$–C$_6$H$_2$	60	96
17	I	H	4-Et–C$_6$H$_4$	40	97
18	Br	4-Ac	3,4,5-F$_3$–C$_6$H$_2$	50	96
19	Br	4-Ac	4-Et–C$_6$H$_4$	40	96
20[a])	Br	4-CN	4-Et–C$_6$H$_4$	40	97
21[a])	Br	4-CN	3,4,5-F$_3$–C$_6$H$_2$	50	90
22	Br	4-OH	4-Et–C$_6$H$_4$	45	95
23	Br	4-OH	3,4,5-F$_3$–C$_6$H$_2$	50	90
24	Cl	4-CN	3,4,5-F$_3$–C$_6$H$_2$	70	90
25	Cl	4-CN	4-Et–C$_6$H$_4$	55	95

[a]) Reactions conducted in H_2O/EtOH 1:1 (1 ml) under reflux. [b]) Yield of isolated product.

Table 7. *Comparison of Activities of Different Catalysts in the* Suzuki *Reaction*[a])

Entry	Catalyst	Reaction Conditions	Time	Yield[b]) [%]	Ref.
1	Nano Pd/Al$_2$O$_3$ (0.1 mol-%)	NMP, Na$_2$CO$_3$, H$_2$O, Ar flow, 65°	3 h	72	[12a]
2	Nano Pd/chitosan (0.5 mol-%)	K$_3$PO$_4$, Bu$_4$NBr (TBAB), H$_2$O, MW, 150°	5 min	98	[12b]
3	Pd/SiO$_2$–TiO$_2$ (0.05 mmol)	K$_2$CO$_3$, EtOH, 78°	6 h	91.3	[12c]
4	Pd–NHC/hybrid silica[c]) (0.2 mol-%)	K$_2$CO$_3$, DMF/H$_2$O, 110°	30 min	96	[12d]
5	Pd–Phosphine/SiO$_2$ (0.025 g)	K$_2$CO$_3$, MeOH/H$_2$O, r.t.	48 h	87	[12e]
6	SS-Pd[d]) (2 mol-%)	K$_2$CO$_3$, DMF, 110°	10 h	85	[12f]
7	Nano Pd/ZnO (925 · 10^{-9} mol-%)	K$_2$CO$_3$, H$_2$O, 100°	30 min	96	This study

[a]) See *Scheme*. [b]) Yield of isolated product. [c]) Hybrid silica-based catalyst derived from Pd–NHC (*N*-heterocyclic carbenes) complexes. [d]) Solid-supported nano- and microparticles of Pd^0 (SS-Pd).

Table 8. *Recycling of the Catalyst in the Reaction of 1-(4-Bromophenyl)ethanone with Phenylboronic Acid in the Presence of Pd/ZnO Nanoparticles*[a])

Run	1	2	3	4	5	6	7
Time [min]	30	35	35	37	40	40	45
Yield[b]) [%]	96	95	95	95	94	94	94

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), phenylboronic acid (1 mmol), Pd/ZnO nanoparticles (0.001 g), H$_2$O (1 ml), K$_2$CO$_3$ (0.25 mmol), 100°. [b]) Yield of isolated product.

To show the merit of this catalytic method, we compared our results with similar data published by other groups which used other catalysts (*Table 7*). Having established the efficacy of Pd/ZnO nanoparticles in *Suzuki*-coupling reactions, we then investigated the recyclability of the catalyst in the reaction of 1-(4-bromophenyl)ethanone with phenylboronic acid in H$_2$O (*Table 8*). Pd/ZnO could be reused successfully for ten runs without either significant loss of yield or extension of the reaction time. The first reaction was carried out within 30 min. Similarly, the repeated runs of the reaction were conducted. After appropriate time, the mixture was centrifuged to separate the catalyst. Then, it was washed with AcOEt (5 ml) and H$_2$O (5 ml) and dried *in vacuo* for the next cycle. The results indicate that only 0.02 wt% Pd were leached out from the catalyst surface after seven cycles (the initial 9.84 wt% Pd decreased to 9.82 wt%).

The XRD pattern (*Fig. 6,a*) and TEM image (*Fig. 6,b*) of the recovered nano catalyst after the 7th run showed that no significant aggregation of the particles has occurred and the morphology and the size of the particles were not disturbed notably in comparison with the TEM picture of the catalyst before the reaction. This observation confirmed that Pd/ZnO nanoparticles were stable under the reaction conditions and were not affected by the reactants.

Also, the heterogeneity of the catalyst was evaluated to study whether the reaction used solid catalysts or was catalyzed by nano Pd/ZnO species in the liquid phase. To address this issue, two separate experiments were conducted with 1-(4-bromophen-
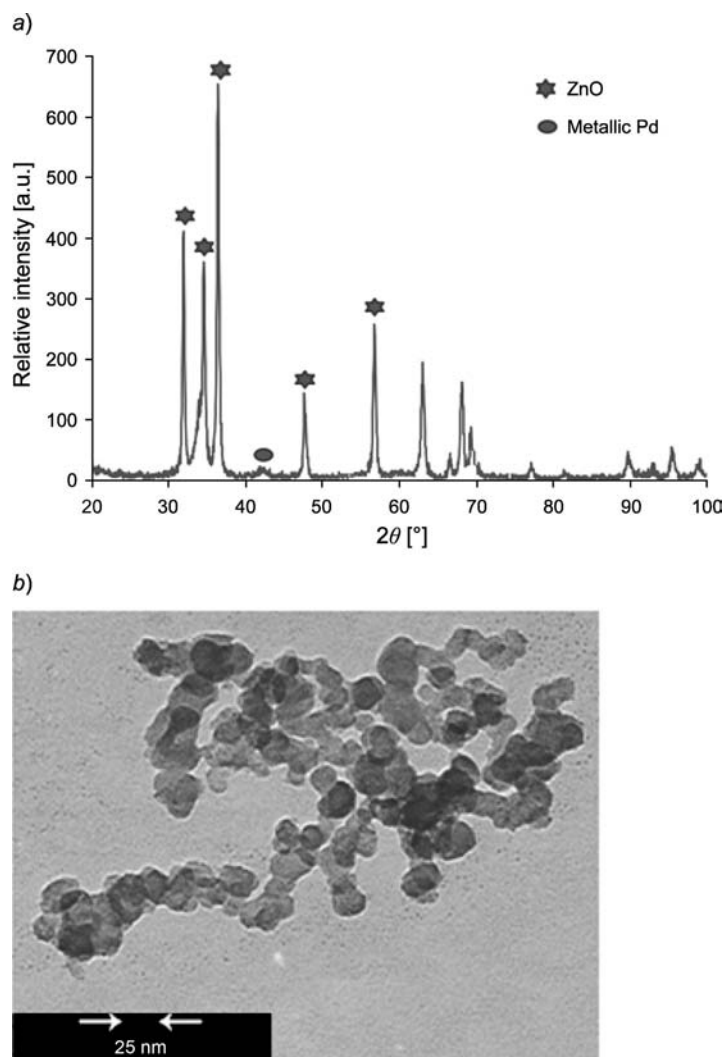
Fig. 6. a) *XRD and* b) *TEM images of Pd/ZnO nanoparticles used for the reaction of 1-(4-bromophenyl)ethanone with phenylboronic acid, after the 7th run recycling of the catalyst*

yl)ethanone (1 mmol) and phenylboronic acid (1 mmol). In the first experiment, the reaction was terminated after 15 min; at this point, the catalyst was separated from the mixture by centrifugation, and the reaction was continued with the filtrate for additional 5 h. In the second experiment, the reaction was terminated after 15 min. In both cases, the desired product was obtained in the same yield (48%). Pd was not detected in the filtrate in either experiment by ICP analysis. This observation confirms that Pd/ZnO nanoparticles are stable under the reaction conditions and behave indeed as heterogeneous solid catalyst [13].

Driven by the results of the *Suzuki–Miyaura* coupling reaction, we further explored the application of the nano Pd/ZnO catalyst in another important C–C bond forming reaction, namely *Hiyama* cross coupling of aryl halides with trimethoxy(phenyl)silane. At first, the *Hiyama* cross-coupling reaction between 1-(4-bromophenyl)ethanone (1 mmol), trimethoxy(phenyl)silane (1 mmol), and K_2CO_3 (1 mmol) as base in the presence of Pd/ZnO (0.009 g), in H_2O as solvent was studied, *i.e.*, the reaction conditions were the same as those for the *Suzuki–Myaura* coupling described above. The obtained yields under these conditions were low, but the *Hiyama* cross coupling could be improved in light of the results of solvent screening as shown in *Table 9*. Using ethane-1,2-diol as solvent gave satisfactory results, whereas the use of other protic and aprotic polar solvents, which are commonly used in Pd-catalyzed coupling reactions, was not effective (*Table 9, Entries 3–8*). The bases were screened as well. According to the results shown in *Table 9* (*Entries 2 and 10–12*), K_2CO_3 was chosen as base in terms of cost (*Entry 2*), although K_3PO_4 led to an excellent yield as well (*Entry 10*). In addition, the effect of temperatures was also studied, and the results are shown in *Table 9* (*Entries 2 and 13–16*). The results indicate that the best temperature under the applied reaction conditions was 100° for 1 h reaction time (*Entry 2*).

Similar to the *Suzuki* reaction, we continued our studies and optimized the amount of Pd/ZnO catalyst for the *Hiyama* coupling reaction after selection of the best solvent

Table 9. *Effects of Solvents, Bases, and Temperature on the* Hiyama *Coupling Reaction*[a])
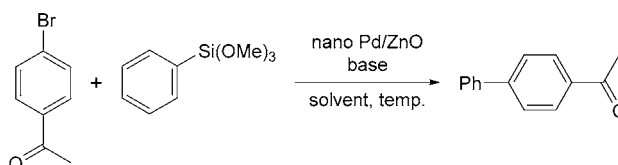
Entry	Solvent	Base	Time [h]	Temp. [°]	Yield[b]) [%]
1	H_2O	K_2CO_3	5	100	15
2	Ethane-1,2-diol	K_2CO_3	1	100	95
3	EtOH	K_2CO_3	5	100	60
4	PEG-300	K_2CO_3	5	100	80
5	PEG-2000	K_2CO_3	5	100	35
6	1,4-Dioxane	K_2CO_3	5	100	None
7	DMSO	K_2CO_3	5	100	25
8	DMF	K_2CO_3	5	100	20
9	None	K_2CO_3	5	100	None
10	Ethane-1,2-diol	K_3PO_4	5	100	95
11	Ethane-1,2-diol	KOH	5	100	90
12	Ethane-1,2-diol	Na_2CO_3	5	100	90
13	Ethane-1,2-diol	K_2CO_3	1	80	95
14	Ethane-1,2-diol	K_2CO_3	4	50	85
15	Ethane-1,2-diol	K_2CO_3	10	40	75
16	Ethane-1,2-diol	K_2CO_3	24	r.t.	30

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), trimethoxy(phenyl)silane (1 mmol), base (1 mmol), Pd/ZnO nanoparticles (0.009 g), solvent (1 ml). [b]) Yield of isolated product.

and base (*Table 10*). On the basis of the optimized reaction conditions, the coupling reactions between aryl halides and trimethoxy(phenyl)silane were carried out (*Table 11*). The electronic property of the substituent has a strong influence on the reactivity of aryl bromides and chlorides. As shown in *Table 11*, the electron-deficient aryl bromides and chlorides showed an excellent reactivity and furnished the products in high yields after short reaction times (*Table 11*, *Entries 6 – 10*). Furthermore, in the presence of aryl iodides as reactants, substrates with electron-withdrawing or electron-donating groups gave the desired products in good yields (*Table 11*, *Entries 1 – 5*).

To conclude, Pd supported on ZnO has been used as heterogeneous and recyclable catalyst for C–C cross-coupling reactions in H_2O and ethyleneglycol as solvents without using any ligands and under normal atmosphere, *i.e.*, without the need of Ar or N_2 as protecting gas. These reaction conditions allow the easy extractive recovery of the final product, and the solid residue showing catalytic activity can be reused several times. This method will provide a facile, efficient, and environmentally friendly process for *Suzuki* and *Hiyama* reactions because of its wide applicability to various substrates,

Table 10. *Optimization of the Amount of Pd/ZnO in the* Hiyama *Coupling Reaction*[a])

Entry	Pd/ZnO [g, mol-% of Pd[b])]	Time [h]	Yield[c]) [%]
1	0.001, 925 · 10⁻⁹	3	80
2	0.005, 4625 · 10⁻⁹	2	90
3	0.009, 8325 · 10⁻⁹	1	95
4	0.04, 37 · 10⁻⁶	1	95

[a]) Reagents and conditions: 1-(4-bromophenyl)ethanone (1 mmol), trimethoxy(phenyl)silane (1 mmol), ethyleneglycol (1 mmol), K_2CO_3 (1 mmol), and Pd/ZnO, 100°. [b]) Determined by ICP. [c]) Yield of isolated product.

Table 11. Hiyama *Coupling of Aryl Halides with Trimethoxy(phenyl)silane Catalyzed by Nano Pd/ZnO*
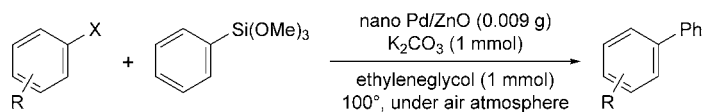
Entry	X	R	Time [min]	Yield[a]) [%]
1	I	H	50	96
2	I	4-MeO	70	85
3	I	4-NO₂	45	94
4	I	2-Me	70	90
5	I	4-NH₂	60	90
6	Cl	4-CN	70	92
7	Cl	4-NO₂	80	91
8	Br	4-OH	45	93
9	Br	4-CN	40	92
10	Br	4-Ac	60	95

[a]) Yield of isolated product.

the use of less toxic reagents, mild reaction conditions, and a small amount of Pd ($925 \cdot 10^{-9}$ mol-%). We believe that this type of nanocrystalline metal oxides will find excellent use as active catalysts not only for laboratory scale research but also for industrial applications.

Experimental Part

General. Reagents and solvents were purchased from *Fluka*, *Aldrich*, *Alfa Aesar*, and *Merck*. Nanoparticles of Pd/ZnO and ZnO were synthesized as reported previously [13]. Evaporation of solvents was performed under reduced pressure with a *Büchi* rotary evaporator. The progress of the reactions was monitored by thin-layer chromatography (TLC) using silica gel *SILG/UV 254* plates (SiO_2). Column chromatography (CC): short columns of *SiO_2 60* (70–230 mesh) in glass columns (2–3 cm i.d.); 15–30 g of SiO_2 per 1 g of crude mixture.

General Procedure for the Synthesis of Pd/ZnO Nanoparticles. Pd/ZnO Catalyst was prepared by CP method. To a mixture of $Pd(NO_3)_2$ (0.027 g ml^{-1}) and $Zn(NO_3)_2$ (0.267 g ml^{-1}) solns., an aq. 1M Na_2CO_3 soln. was added at r.t. until pH 8 was reached. Then, the mixture was kept for 2 h at 70–80°, and the precipitate was filtered, washed several times with dist. H_2O and anh. EtOH, dried at 80° overnight, and then calcinated at 723 K for 2 h [13].

General Procedure for the Synthesis of ZnO Nanoparticles. Nano ZnO catalyst was prepared by CP method. A $Zn(NO_3)_2$ soln. (0.267 g ml^{-1}) was precipitated with 1M Na_2CO_3 soln. at r.t. until pH 8 was reached. After keeping the mixture for 2 h at 70–80°, the precipitate was filtered, washed several times with dist. H_2O, dried at 80° overnight, and then calcined at 723 K for 2 h.

General Procedure for Suzuki–Miyaura *Reaction.* A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), K_2CO_3 (0.25 mmol), and nano Pd/ZnO (0.001 g) in H_2O (1 ml) was added to a round-bottom flask under atmospheric pressure. The mixture was stirred at 100°. The progress of reaction was monitored by TLC. After the reaction was finished, the mixture was cooled to r.t. and diluted with AcOEt (5 ml). The slurry was stirred at r.t. to ensure removal of the product from the surface of the catalyst. Then, it was centrifuged to separate the catalyst. The centrifugate was washed with H_2O (2 × 5 ml), dried (Na_2SO_4), further concentrated under reduced pressure, and purified by CC (SiO_2) to give the desired product. All compounds were characterized by comparison of their physical and spectroscopic data with those reported in the literature.

General Procedure for Hiyama *Coupling Reaction.* A mixture of aryl halide (1 mmol), trimethoxy-(phenyl)silane (1 mmol), K_2CO_3 (1 mmol), and Pd/ZnO (0.009 g) in ethane-1,2-diol (1 ml) was added to a round-bottom flask under atmospheric pressure. The mixture was stirred at 100°. After appropriate time, the mixture was centrifuged to separate the catalyst. Then, it was extracted with AcOEt (5 ml). The combined org. extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by CC (SiO_2) to give the desired product. All compounds were characterized by comparison of their physical and spectroscopic data with those reported in the literature.

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