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Development of a highly active and reusable heterogeneous catalyst based on ZnS-doped Ni (5%) for Suzuki cross-coupling reactions

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Abstract

This paper reports the preparation and characterization of the coupling of aryl halides with arylboronic acids using a new nanomaterial catalyst Ni(5%): ZnS synthesized in the aqueous phase. The X-ray diffraction (XRD) analysis shows the formation of the cubic zinc blende phase, with a particle size of about 3 nm confirmed by high resolution transmission electron microscopy with a high catalytic activity in a water/DMF mixture. However, the ultrasonic activations result in better yields and reaction times. These results prove that the Ni(5%): ZnS nanomaterial is a potential catalyst in the development of green synthesis and that coupling reactions, that proved to be economical, are of paramount importance in industrial applications. In every case, the regioselectivity of the reaction is established on ^{1}H-NMR data. We therefore propose a reaction mechanism that could explain the results obtained.

Keywords: Suzuki Reaction, ultrasonic irradiation; nanomaterial Ni:ZnS, Catalysts, Water, mechanism.

1. Introduction

Palladium nanoparticles (NPs) have diverse applications in the field of both homogeneous and heterogeneous catalysis [1]. Suzuki and Heck reactions are the most important coupling reactions in the synthesis of a wide variety of simple to complex molecules which have many applications in the fields of pharmaceuticals, agrochemicals and advanced materials [2]. Although homogeneous Pd catalysts always exhibit a better reaction rate, activity and selectivity, heterogeneous catalysts have many advantages over their homogeneous counterparts such as recyclability, cost effectiveness and ease of catalyst/product separation [1–2].

Metal nanoparticles are very attractive catalysts compared to bulk catalysts since they have high surface-to-volume ratios and their surface atoms are very active. Numerous review articles have been written on the use of various types of organic and inorganic reactions of noble metal nanoparticles suspended in colloidal solutions and of those adsorbed onto different supports as catalysts. Traditional nanocatalysts include noble metal nanoparticles in colloidal solutions [3], those adsorbed onto bulk supports [4] and lithographically fabricated arrays of nanocatalysts [5]. There are numerous articles on the use of noble metal nanoparticles as catalysts for Suzuki and Heck cross-coupling reactions. Herein, we report nano-size ZnS sphere-shaped particles as anew heterogeneous catalysts for the synthesis of Propargylamines. ZnS has been used as a semiconductor material and is often used as a photo catalyst in the degradation of contaminated water containing halo benzene derivatives, Organic dyes with toxic metal ions [6, 7]. Very recently ZnS has been used as a catalyst for the synthesis of 5-substituted 1H-tetrazoles [8].

The use of ultrasound in organic synthesis has particularly increased in recent years [9-19]. Indeed, the identification of the specific role of ultrasound in organic synthesis has been shown in homogeneous [20] and in heterogeneous media [21]. Ultrasounds are elastic waves that possess all the properties of sound waves such as the disturbance of the medium in which they propagate. The two most evident parameters for the characterization of an alternative pressure wave are frequency, f, (between 16 Hz and 200 MHz) and the amplitude, P.

In a liquid, the action of ultrasounds is mainly based on the phenomenon of cavitation which describes the non-linear oscillation of a gas and/or vapor bubble in a liquid. In this case we are talking about acoustic cavitation [22-25], a phenomenon which causes the chemical transformations observed. Collapsing in on themselves, these cavitation microbubbles release an important amount of energy in the form of intense local heat, very high pressure, shock waves, acoustic microcurrents and microjets [26, 27]. As an approximation, the dynamics of the bubble is a local pressure below the ambient pressure which creates microcavities with a diameter that can reach several tens of micrometers.

Inside the bubble, there are temperatures of approximately 5000 K, pressures of almost 1000 bars, adjacent diverging shocks and violent liquid jets near the solid walls that surround the bubble. The result of these sudden changes in this sonicated medium is highlighted by the increase in temperature of the liquid medium and the formation of free radicals resulting in chemical modifications of said medium. On the other hand, the sonication of biphasic systems [28-33] increases the reaction rate by ensuring better contact between the different phases present. It turns out that, when considering organic synthesis, several chemical reactions have been reanalyzed using this sonochemical activation technique [34-35].

Carbon-carbon coupling reactions induce the formation of bonds between two carbon atoms. This type of reaction has become one of the basic tools of an organic chemist as it provides the possibility of synthesizing very complex molecules. The most important uses are, for example, the preparation of molecules for the pharmaceutical industry [36]. There are many reactions of this type according to the nature of the reactants involved. Recently, a Ni(5%): ZnS catalyst has been used in organic synthesis for the preparation of tetrazoles[6]. In this work we propose the study of the effect of the catalytic system and the ultrasound activation on the evolution of the coupling reaction of aryl halides with arylboronic acids. In addition, we propose reaction mechanisms that could explain the results obtained.

In order to overcome these drawbacks, attention has been paid to the heterogeneous crystals because of the unique properties of nanoparticles. Therefore, the use of a new catalyst with a high catalytic activity and the short reaction time, make the synthesis of a catalyst in green chemistry easier, which is a highly desirable characteristic. It has been reported in the literature that Ni (5%):ZnS, which is a semiconductor material, can be used as a catalyst in the photodegradation of contaminated water containing organic dyes and toxic metals [37, 38]. A nano- Ni (5%):ZnS catalyst was prepared by a simple and efficient single-pot wet chemical technique which provides the large scale production of Ni (5%):ZnS nanoparticles at a low cost and with a high purity.

The characteristic photophysical properties of the Ni^{2+} cation are found between 498 and 520 nm [39-41]. These spectra are similar to those obtained for the undoped ZnS nanocrystals with an emission wavelength of 453 nm.

2. **Experimental**

2.1. *Synthesis of the Ni (5%):ZnS nanomaterial in the aqueous phase*

5 % Ni^{2+}doping Ni:ZnS@2-Mercaptoethanol QDs were prepared as follows: in a three-neck round-bottomed flask, 5 mL of 0.1 M $Zn[OOCCH_3]_2·2H_2O$, 250 µL of 0.1 M $Ni(OCOCH_3)_2·4H_2O$, and 20 mL of 0.1 M 2-Mercaptoethanol were combined. The pH of this solution was adjusted to 10.5 using 2 M NaOH. Next, the solution was degassed by bubbling N_2 gas for 1 h, after which 4.5 mL of degassed 0.1 M thioacetamid (C_2H_5NS) were quickly injected into the solution. The reaction mixture was then brought to reflux. After around 12 h of heating, the solution was cooled down to room temperature.

The nanocrystals were precipitated using i-PrOH, collected by centrifugation, washed 3 times with i-PrOH and then dried in vacuum at room temperature.

2.2. *Classical procedure without ultrasound*

The aryl halide (1.0 mmol), Aliquat-336 (1.25 mmol), $PhB(OH)_2$ (1.5 mmol) and the Ni (5%):ZnS catalyst (0.02 mmol) were placed in a schlenk tube. Vacuum was applied for 30 minutes and argon was then admitted. Water (1.5 mL) and N,N-dimethylformamide (1.5 mL) were added. The reaction was carried out at 100 °C for 5 h (Fig 1). After the reaction, the mixture was cooled and the organic phase was extracted (three times) with water/hexane. It was then dried on $MgSO_4$ and the solvent removed under vacuum. The coupling product was finally isolated by silica gel chromatography.

2.3. *Ultrasonic irradiation*

The ultrasonic probe was immersed directly in the reactor. An ultrasonic generator (Sonics VC 505 300 W) emitted the sound vibration into the reaction mixture. Sonication was achieved at low frequencies of 20 kHz (amplitude of 50%) at room temperature for 5 min. The aryl halide (i1-10) (1.0 mmol), Aliquat-336 (1.25 mmol), $PhB(OH)_2$ (a) (1.5 mmol) and the Ni (5%):ZnS catalyst (0.02 mmol) were placed in a reactor. Water (1.5 mL) and N,N-dimethylformamide (1.5 mL) were added. After the reaction, the mixture was extracted (three times) with water/hexane. The mixture was then dried on $MgSO_4$ and the solvent removed under vacuum. The coupling product was finally isolated by silica gel chromatography. The yields of the reactions were determined by gas chromatography on a Shimadzu 2014-GC apparatus. The capillary column was DB-5 and the carrier gas was helium.

2.4. *Instruments*

The structure of the crystalline phase of the as-synthesized powders was characterized by X-ray diffraction (XRD) on a BRUKER D8 ADVANCE diffractometer using Cu Kα radiation. The particle morphology study was carried out using an FEI Tecnai G2 Transmission Electron Microscope (TEM) operating at 200 kV. The samples were studied using a Philips CM_20 instrument operating at 200 kV equipped with an Energy Dispersive X-ray Spectrometer (EDS).

All compounds were characterized by IR, ^1H NMR spectra, ^{13}C NMR spectra and mass spectra. The IR spectra were recorded in KBr with a JASCO FT-IR-420 spectrometer, with a precision of ±2 cm^{-1} in the 400-4000 cm^{-1} range. The ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were obtained on a Bruker AC300 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts are given in ppm. The coupling products were analyzed by GC-MS (Hewlett-Packard computerized system consisting of a 5890 gas chromatograph coupled with a 5971A mass spectrometer) using fused-silica capillary columns with a polar stationary phase: Supelcowax 10 (60 m- 0.2 mm - 0.20 lm film thickness). GC-MS analyses were obtained using the following conditions: carrier gas He; flow rate 1 ml/min; split 1:20; injection volume 0.1 ll; injection temperature 250 °C; oven temperature programmed from 60 to 220°C at 4 °C/min and holding at 220°C for 30 min; the ionization mode used was electronic impact at 70 eV. Melting points were taken on an Eichert-Heizbank apparatus.

3. **Results and discussion**

In this work we have studied some Suzuki reactions using aryl halides and boronic acids. The isolated product was formed by magnetic stirring or ultrasonic irradiation in the presence of a Ni (5%):ZnS nanoparticle catalytic system. Semiconductor nanocrystals, or quantum dots (QDs), have attracted much attention over the past few years as a novel class of material with unique electronic and optical properties [42-43] and coupling with an interesting catalytic reactivity.

3.1. *Characterization of the Ni (5%):ZnS nanomaterial*

The wide-angle XRD patterns of Ni (5%):ZnS nanocrystals exhibit the (1 1 1), (2 2 0), and (3 1 1) planes as shown in Fig 3, confirming that they are in the cubic zinc blende phase (JCPDS No. 05-0566). The broadness of the peaks is due to the small size of the crystals. No diffraction peaks from impurities were detected in the sample. The diameter of the Ni (5%):ZnS particles was estimated using the Debye-Scherrer formula [38,42]:

$$L=\frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where β is the full width at half maximum (FWHM) of the diffraction peak in radians, ɵ is Bragg's diffraction angle and λ is the wavelength for the Kα1 component of the copper radiation used (1.5418 Å).

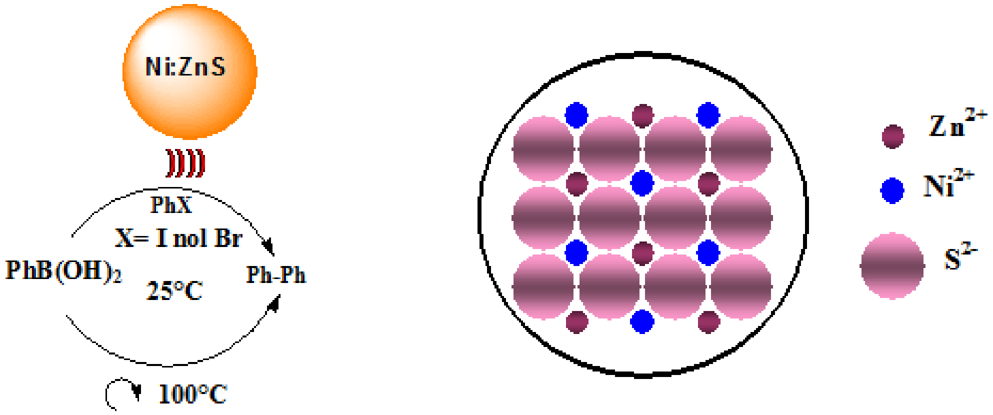


Figure 1. The Suzuki-Miyaura reaction catalyzed by Ni(5%):ZnS (c) under ultrasonic irradiation and magnetic stirring.

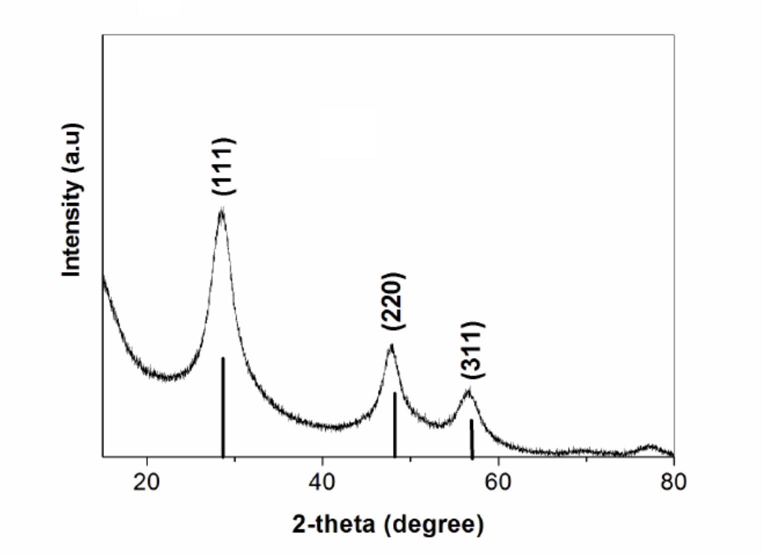


Figure 2: XRD patterns of the Ni(5%):ZnS particle. The line spectrum (bottom) indicates the reflections of the zinc blende

The average size of the Ni:ZnS crystallites was found to be 4 nm. A representative transmission electron microscopy (TEM) image of Ni:ZnS@2-Mercaptoethanol QDs is shown in Fig. 4a. The average size of the nanocrystals is approximately 3.98 ± 0.44 nm, based on statistical analyses of more than 100 nanoparticles in one region (Fig. 3b). As it can be seen, Ni:ZnS@2-Mercaptoethanol QDs are almost monodispersed and spherical in shape.

As an example, the EDX spectrum recorded for the ZnS-doped Ni sample corresponding to a nominal composition of nickel of 5% is shown. This spectrum clearly shows the presence of sulphur, zinc and nickel as the chemical elements present in the solid phase prepared (Fig. 3c).

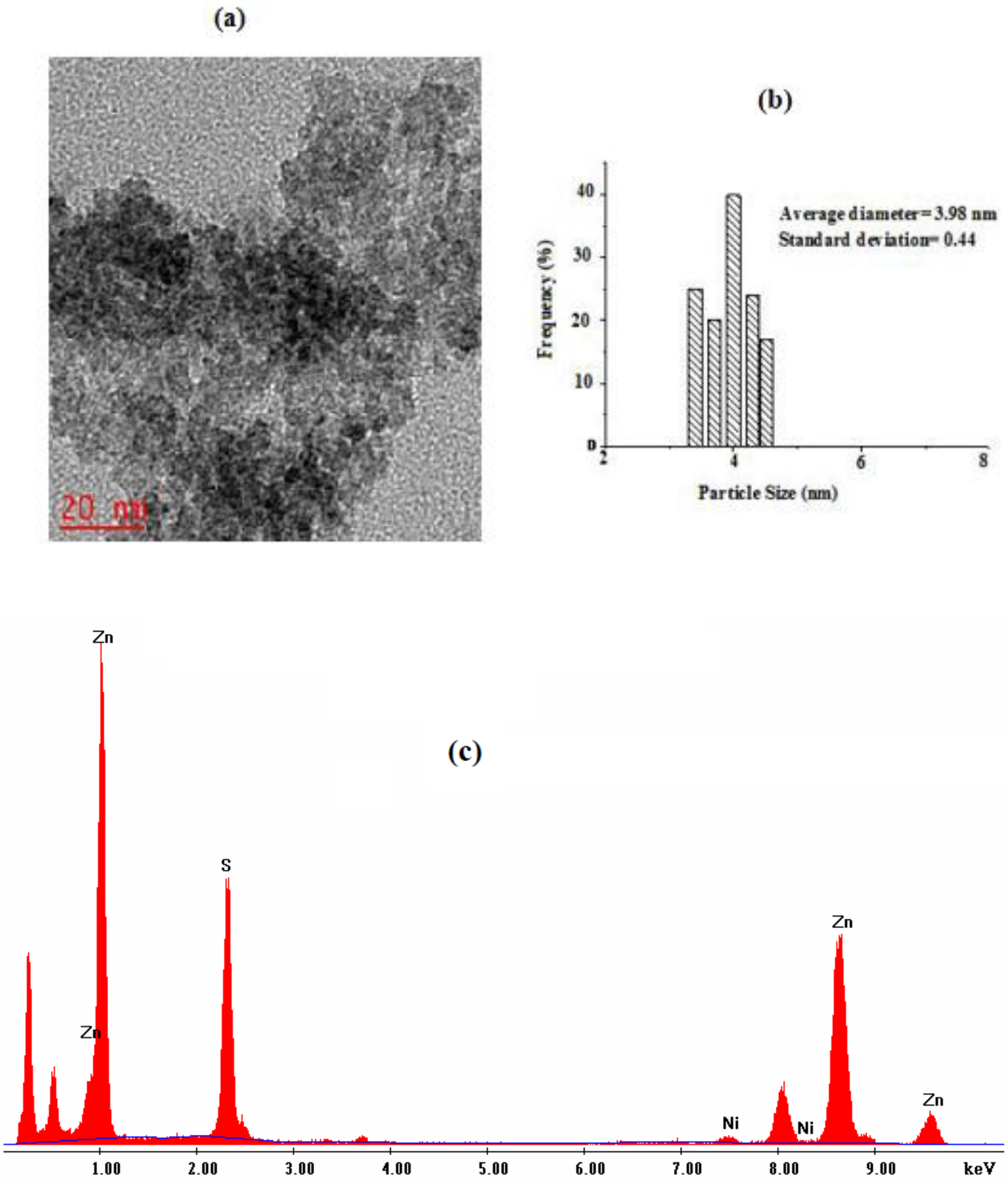


Figure 3. (a) TEM image of Ni(5%):ZnS, (b) the corresponding size distribution and (c) EDX spectrum of the

3.2. Effect of the nature of the halogen in the Suzuki-coupling reaction

In order to test the behavior of the halogen in the Suzuki-coupling reaction, a comparative stage was used in the presence of a new semiconductor material taken from the literature. It was reported that Ni(5%):ZnS is a semiconductor material that can be used as a photo catalyst in the degradation of contaminated water containing halo benzene derivatives, organic dyes and toxic metal ions [43,44]. Recently, the use of a Ni:ZnS catalyst in organic synthesis, that is in the preparation of tetrazoles, has been reported [45]. A nanocatalyst, Ni(5%):ZnS, was prepared by a simple and efficient single-pot wet chemical technique which provides the large scale production of

Ni (5%):ZnS particles at a low cost and with a high purity. The effect of the nature of the halogen in the coupling reaction between aryl halides and aryl boronic acids is shown in Table 1.

Table 1. Effect of the nature of the halogen in the Suzuki-coupling reaction.

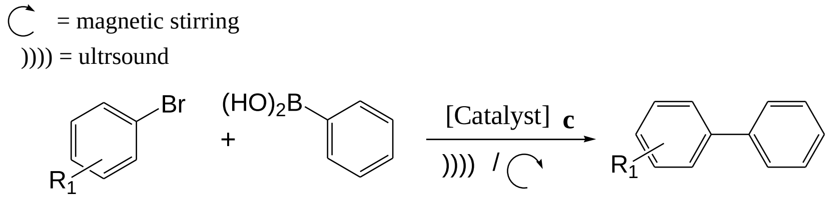
Entry	X	R	Yield (%)[a*]	Yield (%)[b*]	Yield (%)[d,e*]	Lit.
1	I	H	72	89	91[d]	46
2		COMe	70	85	-	
3		NO_2	64	82	-	
4	Br	H	63	83	92[d], 87[e]	46, 47
5		COMe	60	80	91[d], 93[e]	46, 47
6		NO_2	55	75	88	46
7	Cl	NH_2	35	45	-	
8		H	36	40	-	
9		COMe	27	37	-	

[a] Reaction condition aryl halide (0.5 mmol), $PhB(OH)_2$ (0.75mmol), Cs_2CO_3 (1.0mmol), catalyst **c** (1% mmol**),** Water (2 mml) and DMF (2 mml), at 5 h for 100 °C.
[b] Aryl halide (0.5 mmol), $PhB(OH)_2$ (0.75mmol), Cs_2CO_3 (1.0mmol), catalyst **c** (1% mmol**),** water (1.5 mL) and DMF (1.5 mL) Ultrasonic irradiation 5 min at 25°C.
[d] $Ni(OAc)_2$.
[e] $Pd(OAc)_2$.
* Isolated yields.

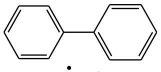
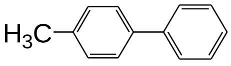
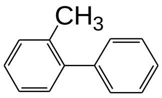
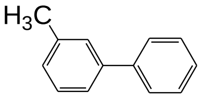
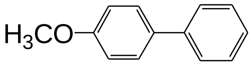
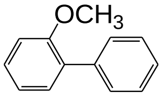
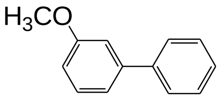
The reactivity of the aryl halide is a function of the halogen atom electronegativity. Therefore, the nature of the halogen has an important effect on the rate of addition of the oxidant. Littke et *al.* [48] showed the relative rates of the oxidant addition with different substituents. This trend can be correlated with various physical parameters of the carbon-halogen bond such as the dissociation energy and interatomic distance [49-51]. A bond that breaks easily corresponds to a greater reactivity of the aromatic halide in a reduction reaction. Nevertheless, chlorine derivatives are still interesting due to the wide variety of available derivatives. Many catalyst systems, such as the Ni (5%):ZnS nanoparticle catalyst used for the synthesis of biaryl (the use of which has been extended to the reaction of various aryl halides and boronic acids (Table 1), have been developed using the Suzuki reaction [52, 53]. Halogenated derivatives are activated by the presence of an electron-withdrawing group and are therefore more reactive during the addition of the oxidant than those having an electron donating group [54]. These aryl halides are brominated or chlorinated and para-substituted with groups having different electronic effects (mesomeric donors: OMe, NH_2; and mesomeric attractors: COMe, COH, NO_2, CN).

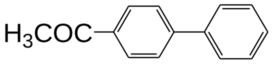
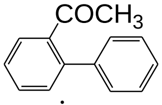
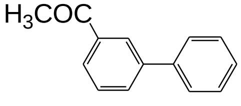
In conclusion, Ni(5%):ZnS particles have been synthesized as a new heterogeneous catalyst with a superior catalytic activity for the synthesis of biaryls and their derivatives with short reaction times and without using an acidic catalyst, solvent or toxic materials. In addition, nano- Ni (5%):ZnS offers the competitive advantage of easy separation from the reaction mixture which means it can be reused. The recyclability of the catalyst showed no significant degradation in catalytic activity. These results proved that the Ni (5%):ZnS catalyst used in the preparation of biaryl provides a development in green synthesis and the reaction is economical and potentially valuable for industrial applications.

Table 2. Suzuki coupling of aryl halides and phenylboronic acid, catalyzed by **c** under ultrasonic irradiation and magnetic



i_{1-10} **a** **i_{1-10}-a**

Entry	ArBr (R_1-C_6H_4Br)	Product	Yield (%)^{a*}	Yield (%)^{b*}	Yield (%)^{d,e*}	Lit.
1	C_6H_5Br **I_1**	 **i_1-a**	68	75	-	-
2	*p*-CH_3 C_6H_4Br **i_2**	 **i_2-a**	50	71	82^d	46
3	*o*-CH_3 -O-C_6H_4Br **I_3**	 **i_3-a**	81	86	72^d	47
4	*m*-CH_3 -O-C_6H_4Br **I_4**	 **i_4-a**	79	90	-	-
5	*p*-CH_3 –O-C_6H_4Br **i_5**	 **i_5-a**	35	81	87^d	47
6	*o*-Me-CH_3 -C_6H_4Br **I_6**	 **i_6-a**	43	55	77^d	46
7	*m*-CH_3.O.C_6H_4Br **i_7**	 **i_7-a**	52	69	82^d	46

8	p-CH_3 OC-C_6H_4Br $\mathbf{i_8}$	 $\mathbf{i_8}$-**a**	80	95	92^e	47
9	o-CH_3OC- C_6H_4Br $\mathbf{i_9}$	 $\mathbf{i_9}$-**a**	50	65	-	-
10	p-CH_3-OC -C_6H_4Br $\mathbf{i_{10}}$	 $\mathbf{i_{10}}$-**a**	58	70	-	-

[a]Reaction conditions: Catalyst **c** (0.02 mmol) ArBr (**1** mmol), $ArB(OH)_2$ (1.5 mmol), Cs_2CO_3 (1 mmol), water (1.5 mL) and DMF (1.5 mL) at 5 h for 100 °C.
[b]Catalyst **c** (0.02 mmol), ArBr (1 mmol), ArB $(OH)_2$ (1.5 mmol), water (1.5 mL) and DMF (1.5 mL) Ultrasonic irradiation 5 min at 25°C.
[d] $Ni(OAc)_2$.
[e]$Pd(OAc)_2$.
* Isolated yields.

The scope of aryl halides and arylboronic acids was studied for the Suzuki cross-coupling reaction in water/DMF mixtures using Ni (5%):ZnS under aerobic conditions. Representative results are summarized in Table 2. The Ni (5%):ZnS complex efficiently catalyzed the coupling of bromobenzene ($\mathbf{i_1}$) with phenylboronic acid. Thus, the Suzuki cross-coupling was carried out with Cs_2CO_3 in the presence of Ni (5%):ZnS in water to give biphenyl ($\mathbf{i_{1\text{-}a}}$) with a 75% yield (Table 2, entry 1). The Suzuki cross-coupling reaction of phenylboronic acid (a) with bromobenzene ($\mathbf{i_{1\text{-}10}}$) derivatives ($\mathbf{i_1}$) bearing electron-donating and withdrawing substituents at their para-positions produced p-methylbiphenyl ($\mathbf{i_2}$), p-methoxybiphenyl ($\mathbf{i_5}$) and p-acetylbiphenyl (i_8) with yields of 71%, 81%, and 95%, respectively (Table 2, entries 2,5 and 8). The coupling reaction of meta- and ortho-substituted bromobenzene derivatives ($\mathbf{i_3}$) and ($\mathbf{i_4}$) having meta-methyl and ortho-methyl groups took place with phenylboronic acid (**a**) to produce 2-methylbiphenyl ($\mathbf{i_{3\text{-}a}}$) and 3-methylbiphenyl ($\mathbf{i_{4a}}$), with yields of 86% and 90% respectively (Table 2, entries 3 and 4).

Ultrasonic irradiation significantly promotes the Suzuki reaction by enhancing both within short reaction times. The reaction medium seems to play an important role under sonication. Water/DMF mixtures are particularly appropriate probably due to the presence of water which favors cavitation [55, 56]. The phenomenon consists in the formation of bubbles within the liquid with their collapse producing high local energies. The bubbles serve in fact as chemical microreactors [57, 58].

Biphenyl ($\mathbf{i_{1\text{-}a}}$). ^1H-NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, 4H, 3J = 7.3 Hz), 7.51 (m, 4H), 7.41 (m, 4H). ^{13}C NMR (100 MHz, CDCl3) δ: 141.70, 128.10, 127.14, 127.09.
MS: 154 (M^+), 76.
4-Methylbiphenyl ($\mathbf{i_{2\text{-}a}}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.66-7.25 (m, 9H); 2.48-2.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.41, 138.6, 137.44, 129.75, 129.07, 127.2, 127.17, 21.39; MS: 168 (M^+), 152.
2-Methylbiphenyl ($\mathbf{i_{3\text{-}a}}$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 7.6 Hz, 2H), 7.38-7.31 (m, 3H), 7.27-7.21 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.39, 142.29, 135.7, 130.77, 130.17, 129.64, 128.54, 127.62, 127.22, 126.14, 20.15; M^+: 168.09.
3-Methylbiphenyl ($\mathbf{i_{4\text{-}a}}$). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.37 (m, 9H); 2.32-2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.31, 142.21, 135.61, 130.69, 130.00, 129.42, 128.33, 127.57, 127.08, 126.09, 20.74; MS: 168 (M^+), 165, 153.
4-Methoxylbiphenyl ($\mathbf{i_{5\text{-}a}}$). ^1H-NMR (400 MHz, $CDCl_3$) δ: 7.59 (m, 2H), 7.55 (m, 2H), 7.49 (t, 2H), 7.33 (t, 1H), 7.28 (dd, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.11, 140.82, 133.73, 128.77, 128.45, 126.72, 126.60, 114.24, 55.39. MS: 184 (M^+), 169, 141, 115, 63.

2-Methoxybiphenyl (**i$_{6\text{-}a}$**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.56 (d, 2H); 7.48-7.42 (t, 2H); 7.39-7.33 (t, 3H); 7.09-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.82, 138.81, 131.24, 131.00, 129.84, 128.95, 128.22, 127.20, 121.19, 111.67, 55.88; MS: 184 (M^+), 169, 141, 115.

3-Methoxybiphenyl (**i$_{7\text{-}a}$**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.64 (m, 2H); 7.55-7.45 (m, 2H); 7.43-7.37 (m, 2H); 7.25-7.21 (m, 2H); 6.98-6.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.32, 143.13, 141.44, 130.01, 129.01, 127.77, 127.58, 119.95, 113.22, 112.93, 55.57; MS: 184 (M^+), 154, 141, 115.

4-Acetylbiphenyl (i$_{8\text{-}a}$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09-8.05 (m, 2H), 7.70-7.62 (m, 4H,), 7.51-7.34 (m, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.94, 146.04, 140.41, 136.11, 129.27, 129.11, 128.15, 127.15, 127.40, 26.81; MS: 196 (M^+), 181, 152, 76, 43.

2-Acetylbiphenyl: (**i$_{9\text{-}a}$**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.49 (m, 4H); 7.46-7.38 (m, 3H); 7.36-7.32 (m, 2H); 2.11-1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.00, 141.21, 140.92, 140.83, 130.91, 130.54, 129.11, 128.90, 128.10, 127.71, 30.62; MS: 196 (M^+), 181, 152.

3-Acetylbiphenyl (**i$_{10\text{-}a}$**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21-8.19 (m, 1H); 7.96-7.92 (m, 1H); 7.79-7.76 (m, 1H); 7.65-7.60 (m, 2H); 7.57-7.45 (m, 3H); 7.41-7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.20, 141.91, 140.42, 137.90, 131.91, 129.33, 129.24, 128.11, 127.41, 127.21, 26.92; MS: 196 (M^+), 181, 152.

Conclusions

In conclusion, Ni(5%):ZnS nanoparticles have been synthesized as a new heterogeneous catalyst with a higher catalytic activity for the Suzuki-Miyaura coupling. This Ni(5%):ZnS complex has proved to be a good catalyst for this reaction since it allows to achieve excellent coupling yields in a very short time and with low catalyst loads. These results prove that the Ni(5%):ZnS nanoparticle catalyst used in the preparation of biaryl is a development in green synthesis with an economical reaction which is potentially valuable for industrial applications.

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References

1. Amarajothi D., Asiric A.M., Garcia H., *Chem. Soc. Rev*. 44 (2015) 1922.
2. Rivera F.G., Angurell I., Rossell M.D., Erni R., Llorca J., Divins N.J., Muller G., Seco M., Rossell O., *Chem.–Eur. J*. 19 (2013) 11963.
3. Xie J., Chen K., Chen X., *Nano Res*. 2 (2009) 261–278.
4. Thibault-Starzyk F., DaturiM., Bazin P., Marie O., *Wiley-VCH: New York. NY. USA*. (2008) 505.
5. Eppler A., Rupprechter G., Guczi L., Somorjai G.A., *J. Phys. Chem. B*. 101 (1997) 9973.
6. Hu J.S., Ren L.L., GuoY.G., Liang H.P., Cao A.M., Wang L.J., Bai C.L., *Angew. Chem.Int. Ed*. 44 (2005) 1269.
7. Bang J.H., Helmich R.J., Suslick K.S., *Adv. Mater*. 20 (2008) 2599.
8. Leiming L., L. Baojun, I. We, J. Liu, X. Li, Y.I. Zheng., *Chem. Commun*. 46 (2010)448.
9. Jianying L., Ming Z., Chenghu X., Shengyu L., Xueqiao Z, Yaoqiang C., C. *Chin. J. Cat*. 34 (2013) 751.
10. Zhang J., Yang F., Ren G., Mak T,C.W., Song M., Wu.Y, *Ult. Sonochem.* 15 (2008) 115.
11. Nagira T., Nakatsuk N., Yasud H., Uesugi K., Takeuchi A., Suzuki Y. *Mater. Let.* 150 (2015) 135.
12. Zhou M., Hu L., *Ultrasonics.* 60 (2015) 76.
13. Tang J., Yan C., Sun L., *Science.* 70 (2016)115.
14. Kulkarni K., Friend J., Yeo L., Perlmutter P., *Ultr. Sonochem.* 21 (2014) 1305.
15. Azizi-Toupkanloo H., Goharshadi E.K., Nancarrow P., *Adv. Pow*. Tech. 25 (2014)801.
16. Skorb E., Möhwald V.H., *Ultrasonics Sonochemistry*. 29 (2016) 589.
17. Di Michele A., Diodati P., Morresi A., Sassi P. *Ultrasonics Sonochemistry.* 16 (2009) 141.
18. Shi-Ying J., Jin H., Shi-Xiao J., Qing-Yuan L., Jin-Xia B., Hong G., *C. Chin J .Nat. Medi*. 12 (2014) 0071.
19. Qiu M., Lianjie Z., Tongtong Z., Hongbin L., Youguang S., Kun L., *Materials Res. Bul*. 47 (2012) 2437.

20. Shaozhong L., Zhang W., Fengxi C., Rong C., *Res. Bul*. 61 (2015) 165.
21. DaMeng Z., Zhu L., tullah K., ShuY, Sun Q., Jang W., Chuno W., *Res. Bul*. 49 (2014) 272.
22. Margulis M., *High Energy Chem.* 38 (2004) 135.
23. Cella R., Stefani H. A., *Tetrahedron.* 62 (2006) 5656.
24. Diodati P., Giannini G., Sacchetti F., *Ult. Sonoch*. 9 (2002) 215.
25. Radziuk D.V., Shchukin D.G., Möhwald H., *Ult. Sonoch. 18(2011) 853*.
26. Krasulya O., Bogush V., Trishina V., Potoroko I., Khmelev S., Sivashanmugam P., Anandan S., *Ult. Sonoch*. 30 (2016) 98.
27. Graves J. E., Sugden M., Litchfield R. E., Hutt D. A., Mason T. J., Cobley A. J., *Ult. Sonoch*. 29 (2016) 428.
28. Moussaoui Y., Saïd K., Ren Salem R., *ARKIVOC* xii. (2006)1.
29. Mhamdi L., Bohli H., MoussaouiY., Ben Salem R., *Inter. J. Org. Chem*. 1 (2011) 119.
30. Moussaoui, Y., Ben Salem, R., *C. R. Chimie*. 10 (2007) 1162.
31. Said K., Moussaoui Y., Kammoun M., Ben Salem R., *Ultr. Sonoch.* 218 (2011) 23.
32. Said K., Moussaoui Y., Ben Salem R., *J. So. Chem.Tu*. 11 (2009) 59.
33. Slimi H., Saïd K., Moussaoui Y., Ben Salem R., *Inte. J. Org. Chem*. 3 (2013)96.
34. Cravotto G., Borretto E., Oliverio M., Procopio A., Penoni A., *Cat. Comm.* 63 (2015) 2.
35. Palmisano G., Tibiletti F., Penoni A., Colombo F., Tollari S., Garella D., Tagliapietr S., *Ultr Sonochem*. 18 (2011) 652.
36. Patil R., Bhoir P., Deshpande P., Wattamwar T., Shirude M., Chaskar P., *Ultr. Sonochem*. 20 (2013) 1327.
37. Bang H. J., Helmich J. R., Suslick K. S., *Adv. Mater*. 20 (2008)2599.
38. Yue Z., Liang X., Langchen L., *Mat. Let.* 64 (2004)1521.
39. Efros L., Rosen M. A., *Annu Rev. Mater. Sci.* 30 (2000) 475.
40. Warner J.H., Tilley R.D ., *Adv. Mater*. 17 (2005) 2997.
41. Ph. K. Sung, Y. Ch. Myong, Ch. Choi. Hyun, *Mat. Rese. Bull*. 74 (2016) 85.
42. Fernando J.V.E. Oli., Melo Jr. Maurıcio A., *Materi. Rese. Bull*. 48 (2013)1045.
43. Peter B., Maria J. S., Matej B., Anna Z., Pavol H., Jr Jaroslav K., Jaroslav K., Erika D., Gabriela M.V., Jan M., *Materi. Rese. Bul*. 49 (2014) 302.
44. Lang. L., Li B., Liu W., Jiang L., Xu Z., Yin G., *Chem. Commun*. 46 (2010) 448.
45. Said K., Labiadh H., Lahbib K. Ben Salem R., *Mediterranean Journal of Chemistry. 5 (2016) 465.*
46. Said K., Ben Salem R., *Advances in Chemical Engineering and Science. 6 (2016) 111.*
47. Littke A. F., Dai C., Fu G. C., *J. Am. Chem. Soc*. 122 (2000) 4020.
48. Artaud I., Seyden-Penne J., Viout P., *Tetra-hedron Letters*. 21 (1980) 613.
49. Fuqiang G., Hongfei L., Zhang Z., Shulan M., Deqian L., *Mate. Rese. Bul*. 66 (2015) 186.
50. Ballini R., Bosica G., *J. Org. Chem*. 355 (1998).
51. Rana S., Maddila S., Yalagala K., Jonnalagadda B.S., *Ap. Cat A: General*. 505 (2015) 539.
52. Lu Z., Fu G.C., *Angew. Chem., Int. Ed*. 49 (2010) 6676.
53. Miyaura N., Suzuki A., *Chem. Rev*. 95 (1995) 2457.
54. Margulis A., *H. Energ. Chem.* 38 (2004) 135.
55. Lorimer J. P., Mason T., *J. Chem. Soc. Rev*. 16 (1987) 239.
56. Luche J. L., Damiano J. C., *J. Am. Chem. Soc*. 102 (1980) 7926.
57. Zhang L., Geng M., Teng P., Zhao D., Lu X., Li J., *Ult. Sonoch*. 19 (2012) 250.