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SYNTHESIS AND CHARACTERISATION OF REUSABLE PVA-SODIUM ALGINATE-Ni CATALYST IN HECK REACTION

(Sintesis dan Pencirian Pemangkin yang Boleh Digunakan Semula dalam Tindak Balas Heck)

Norul Azilah Abdul Rahman[1,2], Nurul Afiqah Mohd Haris[1], Karimah Kassim[3], Mazni Musa[1], and Nur Rahimah Said[1*]

[1]*School of Chemistry and Environment, Universiti Teknologi MARA (UiTM), Cawangan Negeri Sembilan, Kampus Kuala Pilah, 72000 Kuala Pilah, Negeri Sembilan, Malaysia*
[2]*School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*
[3]*Institute of Science (IOS), Level 3, Block C, Kompleks Inspirasi, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia*

[*]*Corresponding author: nurra1435@uitm.edu.my*

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Abstract

Heck reaction is a carbon-carbon coupling reaction that essential for the development of natural products, agrochemicals, optical devices and drugs. During the synthesised of chemicals, the presence of catalysts is important. Normally, the reaction is carried out with the presence of palladium metal as catalyst. However, it has disadvantages such as high toxicity and considerably expensive. Compared to palladium, nickel represent a low cost and environmental friendly type metal. Therefore, nickel is effective to replace the palladium in their application as catalyst in Heck reaction. This study produced a Polyvinyl alcohol-sodium alginate-Nickel (PVA-SA-Ni) catalyst by using one pot synthesis method in the ultrasound irradiation system. The benefits in producing a catalyst not only is cost effective but also its reusability properties due to the presence of PVA-SA as a support. The PVA-SA-Ni was successfully synthesised and characterised by using FTIR, XRD, FESEM-EDX and AAS. The catalytic performance and reusability of PVA-SA-Ni was investigated in Heck reaction between 1-bromo-4-nitrobenzene and styrene. The percentage conversion rate of reactant to product was determined by using GC-FID. The PVA-SA-Ni showed the best performance in Heck reaction with 74 % conversion by using 1 mmol % in the presence of K_2CO_3 as a base at a temperature of 165 °C, and DMA as solvent within 4 h of reaction time.

Keywords: polyvinyl alcohol, sodium alginate, nickel(II) catalyst, Heck reaction, reusable catalyst

Abstrak

Tindak balas heck ialah tindak balas gandingan karbon-karbon adalah penting untuk pembangunan produk semula jadi, agrokimia, peranti optik dan ubat-ubatan. Semasa bahan kimia disintesis, kehadiran pemangkin adalah penting. Biasanya, tindak balas dilakukan dengan kehadiran logam paladium sebagai mangkin. Walau bagaimanapun, ia mempunyai kelemahan seperti kadar toksik tinggi dan harga yang agak mahal. Berbanding dengan paladium, nikel dilihat sebagai jenis logam kos rendah dan mesra alam. Oleh itu, nikel berkesan untuk menggantikan paladium dalam penggunaannya sebagai pemangkin dalam tindak balas Heck. Kajian ini menghasilkan mangkin Polivinil Alkohol-natrium alginat-Nikel (PVA-SA-Ni) menggunakan kaedah sintesis satu pot

dalam sistem penyinaran ultrabunyi. Terdapat banyak faedah dalam menghasilkan pemangkin ini bukan sahaja efektif dari segi kos tetapi dilengkapi dengan sifat kebolehgunaan semula kerana kehadiran PVA sebagai sokongan. PVA-SA-Ni yang telah berjaya disintesis dicirikan menggunakan FTIR, XRD, FESEM-EDX dan AAS. Prestasi pemangkin dan kebolehgunaan semula PVA-SA-Ni telah disiasat dalam tindak balas Heck antara 1-bromo-4-nitrobenzene dengan stirena. Kadar penukaran peratus bahan tindak balas kepada produk ditentukan dengan menggunakan GC-FID. PVA-SA-Ni menunjukkan prestasi yang baik dalam tindak balas Heck dengan penukaran 74 % dengan menggunakan 1 mmol % pemangkin, kehadiran K_2CO_3 sebagai bes pada suhu 165 °C, dan DMA sebagai pelarut dalam masa 4 jam tindak balas.

Kata kunci: polivinil alkohol, natrium alginat, pemangkin nikel(II); tindak balas Heck, pemangkin yang boleh digunakan semula

Introduction

The Heck reaction is a common practical reaction used in the synthesis of natural compounds, agrochemicals, and medicines. Palladium (Pd) catalysts are commonly used in Heck reaction [1] because of their high catalytic activity, high stability, and the reaction can occur at low temperatures [2]. Nevertheless, the price of Pd metal is expensive and toxic that is harmful to the environment leading to its limitations in industrial applications. An alternative to replace the Pd metal is nickel catalyst. It is cheaper, low toxicity, and good in catalytic activity [3].

The catalytic performance of Ni type catalyst in the Heck reaction is comparable with Pd type catalyst. However, the homogenous Ni catalyst has difficulty separating from the product of Heck. Ni-phosphine ligand also has its drawbacks, whereby phosphine is not cheaper, toxic and needs inert condition because it is sensitive to water and oxygen. Heterogeneous Ni type catalyst is more preferable due to easy recovery at the end of reaction, recyclable, reduce waste of chemical and environmentally friendly [4].

The heterogeneous type of catalyst is designed by the presence of solid polymer support in the structure of catalyst. Amongst the polymers, biodegradable polymers such as chitosan (CS) [5], PVA [6] and sodium alginate (SA) [7] are gaining more attention due to their great advantages. For instance CS is an expensive polymer from polysaccharides, non-toxic, biodegradable, renewable and not soluble in common solvents [5]. Interestingly, CS have OH and NH_2 groups that function as chelating ligand to Ni and other metals [8]. Tang et al. [8] synthesized CS together with carbon nanotube (CNT) to support Ni (CS-CNT-Ni). Excellent catalytic activity of CS-CNT-Ni is reported giving 100% acetylene conversion at 160^{o}C. However, no study on recyclability was reported. Hajipour and Abolfathi [5] also synthesized CS with Ni and triazole (CS-triazole-Ni). The catalytic activity of CS-triazole-Ni was good at above 80% of conversion and the recyclability of catalyst is 5 times without any reduction in rate of conversion.

The PVA is also used as support for the synthesis of heterogeneous Ni type catalyst. PVA is non-toxic, biocompatibility, biodegradable and environmentally friendly [6]. Moreover, the presence of hydroxyl group in PVA structure cause it easy to dissolve in water [9] and also can function as ligand during the complexation [10]. Medjili, et al. [11] synthesized Ni supported catalyst with Cu, PVA and polyaniline (PANI). PVA-PANI-Ni-Cu catalyst was successfully used in removing methylene blue (94%) from 10^{-5} M initial concentration of dye. Lakhdari, et al. [6] also synthesis PVA-PANI-Ni-Cu. They applied the PVA-PANI-Ni-Cu in converting the toxic methanol to less harmful by-products, CO_2 and H_2O.

Sodium alginate (SA) is extracted from brown algae that contain polysaccharides. It is water soluble because it contains carboxyl (-COO^-) and hydroxyl (-OH) functional groups. The -COO^- and -OH functional group can coordinate with metal to form coordination complex. The SA will become a hydrogel when it is cross-link with $CaCl_2$ [12]. Qiao et al. [7] synthesized SA-Ni and used as catalyst for hydrogenation. SA-Ni catalyst has excellent catalytic activity in styrene hydrogenation where it successfully converts 99.9% styrene to ethylbenzene. It also can be reused up to 20 times without loss of initial activity.

Both PVA and SA have good interaction with metals. The properties of SA can be increased by blending with

PVA [13]. Knijnenburg, et al. [14] used PVA-SA to bind with Zn for fertilizer application. While Rahman et al. [15] synthesized PVA-SA-$PdCl_2$ for Heck reaction. The catalytic performance of PVA-SA-$PdCl_2$ for reaction of aryl halides with styrene gives an outstanding result of 100% conversion rate. In addition, the recyclability of PVA-SA-$PdCl_2$ is excellent which is over 11 cycles. PVA-SA as active metal site support has been found in many literatures. As noted, there are yet findings available that emphasising the applications of PVA-SA as polymer support for Ni catalysts. Hence, the current study aimed to synthesise polymer-supported Ni or PVA-SA-Ni catalysts employable in Heck reactions. Moreover, the recyclability and optimum reaction conditions of the catalyst in different parameters were determined. This is a fundamental study to determine the capability of synthesis polymer-supported Ni or PVA-SA-Ni as catalyst in Heck reaction.

Materials and Methods

Materials and instrumentation

Polyvinyl alcohol (PVA, 99+% hydrolysed) (Aldrich), sodium alginate (SA) (Sigma, medium viscosity), nickel(II) chloride ($NiCl_2$) (Aldrich, 99%), nitric acid (HNO_3)(R&M Chemicals, 65%), hydrogen peroxide (H_2O_2, 50%) (Bendosen), calcium chloride ($CaCl_2$) (Sigma Aldrich, 97%), distilled water, styrene (R&M Chemicals, 99%), 1-bromo-4-nitrobenzene (Aldrich, 99%), N,N-Dimethylacetamide (DMA) (R&M Chemicals, 99%), toluene (R&M Chemicals, 99.5%), potassium carbonate (K_2CO_3) (Fisher Scientific, 99.5%), methanol (Sigma-Aldrich, 99%) and sodium acetate (NaOAc) (Sigma-Aldrich) were purchased from standard commercial suppliers and used as received without further purification.

The characteristic of PVA-SA-Ni was characterized by using flame atomic absorption spectroscopy (FAAS), attenuated total reflection-Fourier transform infrared (ATR-FTIR), field emission scanning electron microscope-energy dispersive X-ray (FESEM-EDX), and X-ray diffraction (XRD). The Ni content in PVA-SA-Ni was measured by using FAAS (Perkin Elmer-AAnalyst 400) utilizing a flame approach. The spectra of samples were provided by ATR-FTIR (Perkin Elmer Spectrum 100) analysis and recorded in the range of 650 cm^{-1} to 4000 cm^{-1} by averaging 16 scans numbers at 4 cm^{-1} resolution.

The sample surface analysis was conducted utilizing FESEM-EDX (Hitachi, SU8220). The analysis using a Carl Zeiss electron microscope at 10 kV with 3 k magnification. Diffractogram of the samples by using XRD (Empyrean, PANanalytical). It was recorded over a 2-theta range of 2^o to 50^o by X-ray diffractometer with a angle of 0.02^o min^{-1}. The voltage and current were utilized at 40 kV and 20 mA respectively.

The percentages of conversion rate and turnover number (TON) of reactant determined the catalytic efficiency. The percentage conversion rate and percentage TON were calculated by using equation (1) and (2) below. The data was obtained from Gas Chromatography (GC) (Agilent Technologies, 7890A). The instrument was equipped with an HP-5 capillary column (15 m × 0.25 mm × 0.25 μm) with a flame ionization detector (GC-FID). The microliter samples were injected at 50 °C (held for 1 min) and the final temperature of 250 °C (held for 30 s). The temperature increased at a rate of 15 °C min^{-1}. The flow rate was set at 1.9162 mL min^{-1}.

$$\% \text{ conversion} = \frac{A_{initial} - A_{final}}{A_{final}} \times 100 \quad (1)$$

$$\% \text{ TON} = \frac{\% \text{ conversion}}{\% \text{ catalyst}} \quad (2)$$

Preparation of catalyst

In the preparation of $NiCl_2$ catalyst, the optimum parameter from previous study was used with 1 h ultrasonic synthesise time. The modification method was acquired from a study by Rahman et al. [15].

Catalytic testing

1-bromo-4-nitrobenzene reacts with styrene monomer to produce 1-bromo-4-styrylbenzene in Heck reaction. All chemicals: 1-bromo- 4-nitrobenzene (0.2000 g;1 mmol), styrene monomer (0.2083 g; 2 mmol), Na_2CO_3 (0.2500 g, 2.4 mmol), PVA-SA-Ni catalyst (1.0 mmol%) and DMA (10 mL) as solvents was mixed in a round bottle flask and refluxed at 165 ºC based on the boiling point of DMA solvent whilst being purge with the nitrogen gas

for 1 h. The conversion rate of crude products was analyzed by GC-FID. The Heck reactions were then studied with three parameters, including the effect of different reaction times, solvent, and bases.

Recyclability of catalyst

The catalyst was separated from the reaction mixture after reaction and washed with water and acetonitrile to remove salts and organic residual. The catalyst was then dried in a vacuum oven and subjected to use in a fresh new reaction.

Results and Discussion

Characterization of synthesized compound

This study successfully synthesized PVA-SA-Ni (Figure 1) by using a one-pot ultrasonic method. The color of PVA-SA-Ni obtained is pale green as shown in Figure 2 (transformed from white color of PVA-SA). The amount of Ni is 0.14615 % in 50 mg PVA-SA-Ni was determined by using AAS.

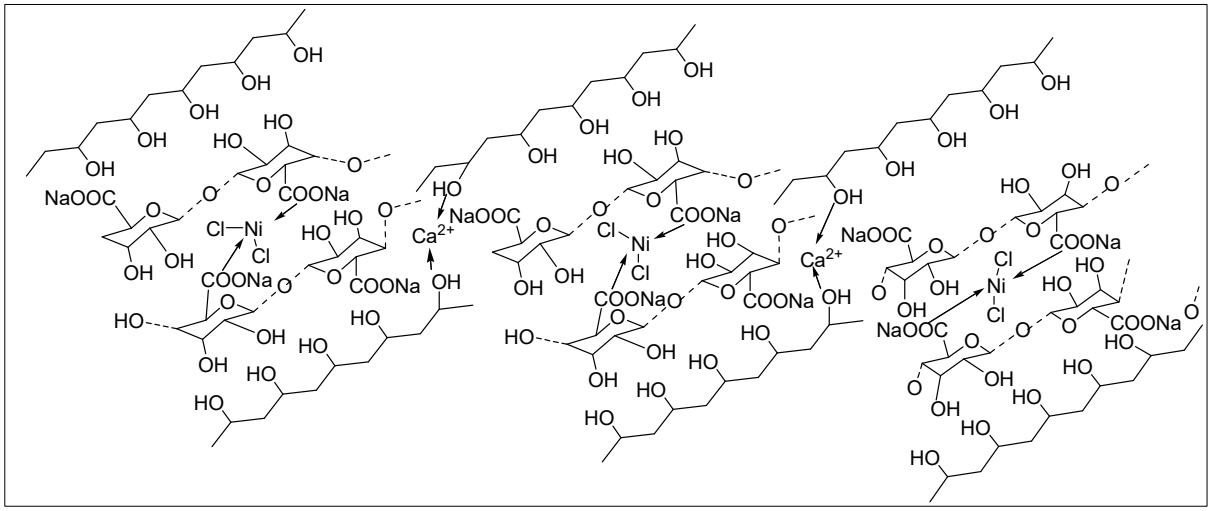


Figure 1. Structure of PVA-SA-Ni

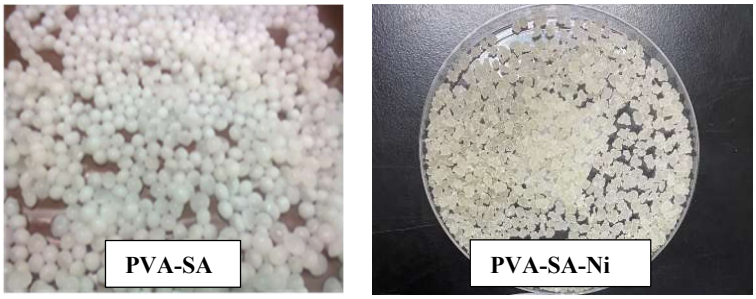


Figure 2. The images of PVA-SA and PVA-SA-Ni

The successful synthesis of PVA-SA-Ni catalyst was confirmed by using ATR-FTIR, FESEM-EDX and XRD. The functional group absorption bands of PVA-SA and PVA-SA-Ni using ATR-FTIR is summarized in Table 1 measured within 650 cm^{-1} to 4000 cm^{-1}. Based on Table 1, the functional group present in PVA-SA and PVA-SA-Ni catalyst is similar. This result showed that the PVA-SA structure was not altered during blending with $NiCl_2$ and only the position of functional group was affected [16].

Table 1 shows no significant changes for hydroxyl (-OH), alkyl (-CH_2 and -CH_3) and -CO groups. The -OH absorption bands appeared at 3345 cm^{-1} and 3355 cm^{-1} in both PVA-SA and PVA-SA-Ni catalyst due to presence of a large amount hydroxyl group in both

structure of PVA and SA [15]. The -CH_2 absorption bands of PVA-SA and PVA-SA-Ni appeared at 2920 cm^{-1} and 2924 cm^{-1}. The group of -CH_3 symmetry bending of PVA-SA and PVA-SA-Ni observed at 1320 cm^{-1} and 1333 cm^{-1}. While the absorption band of -CO visualized at 1085 cm^{-1} and 1086 cm^{-1}. Important absorption band is asymmetric and symmetric vibration of -C=O at 1636 cm^{-1} and 1429 cm^{-1} that moved to lower wavenumbers after complexation due to the interaction of $NiCl_2$ and -C=O from -COONa indicating the successful construction of PVA-SA-Ni catalyst [15, 17].

Table 1. The functional group of PVA-SA and PVA-SA-Ni

Functional Group	PVA-SA (cm^{-1})	PVA-SA-Ni (cm^{-1})
-OH stretching	3345	3355
-CH_2 stretching asymmetric	2920	2924
-C=O asymmetric stretching	1636	1616
-C=O symmetric stretching	1429	1423
-CH_3 symmetric bending	1320	1333
-C-O bending	1085	1086

The micrograph of outer surface and cross-section of PVA-SA and PVA-SA-Ni from FESEM (100x of magnification) is presented in Figure 3. The outer surface and cross section of PVA-SA beads in Figure 3 (A1) and Figure 3 (A2) had a rough and ridged surface. It has pores due to lumps stuck together. The presence of $NiCl_2$ in outer surface and cross section of PVA-SA-Ni Figure 3 (B1) and Figure (B2) caused modification on PVA-SA which resulted more pores on PVA-SA-Ni as compared to PVA-SA [16]. Based on Rahman et al. [15] study's every angle of pores allow catalytic reaction to occur by allowing diffusion of reactant and product utilised in the reaction that help in catalytic activity. The FESEM mapping of PVA-SA-Ni outer surface is shown in Figure 3 (**C1**) and cross-section in Figure 3 (**C2**) revealed that dispersion of Ni metal is homogenous over the whole mass of the beads through the binding process.

Meanwhile, the chemical composition of the PVA-SA and PVA-SA-Ni (Figure 4) was analysised by using an energy dispersive x-ray (EDX). The element present in PVA-SA was similar as reported by Rahman et al. [15] that contain element of carbon (C), oxygen (O), sodium (Na), calcium (Ca) and chlorine (Cl). In contrast, the PVA-SA-Ni detected contained 0.8 % mass of Ni atom. The crystalline phase in PVA-SA and PVA-SA-Ni was confirmed by using XRD as shown in Figure 5. Diffractogram of PVA-SA showed peaks appeared at 20° with shoulder similar to diffractogrom obtained by Sang Joon Lee, et al. [18]. Broad peaks obtained indicated the PVA-SA is in amorphous form similar to a study by Rahman, et al. [15]. In contrast with diffractogram of PVA-SA-Ni , the peaks at 20° is narrower and sharp, indicating that the presence of Ni promoted the crystallisation of PVA-SA [19]. While, peak of Ni at 44.4°, 51.7° and 76.4° [20] was not seen because the amount of Ni in PVA-SA-Ni is small based on data FAAS and EDX. From all the characterisation data of PVA-SA-Ni were sucessfully synthesised and the structure is illustrated in Figure 1.

Catalytic activity of PVA-SA-Ni in Heck reaction

The efficiency of PVA-SA-Ni as catalyst was tested in Heck reaction between styrene and 1-bromo-4-nitrobenzene. The study focused on optimizing the reaction condition and the results are summarized in Table 2. The initial test was conducted by using 1 mmol % of the PVA-SA-Ni catalyst, K_2CO_3 as base, DMA as solvent, reflux at 165 °C temperature based on DMA solvent boiling point with different times. The results are recorded at Entries 1-5.

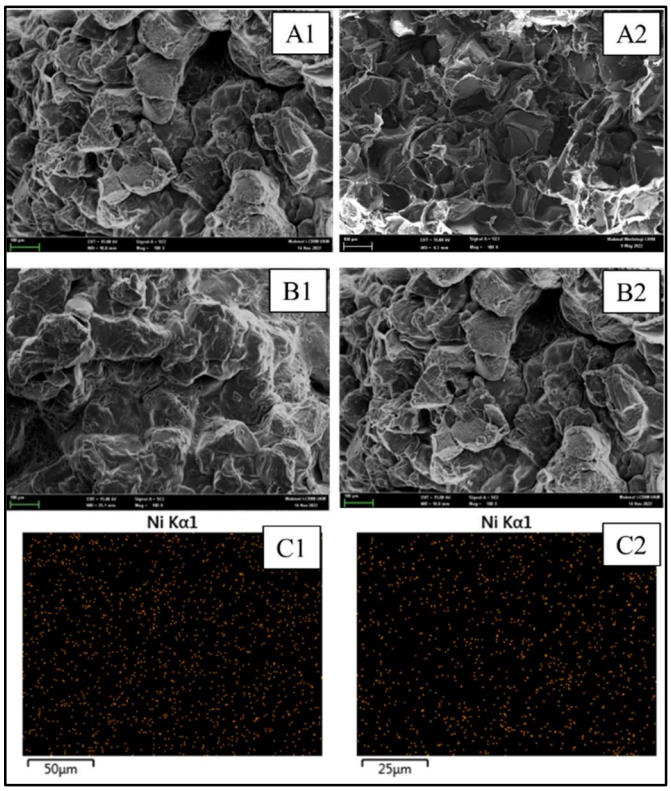
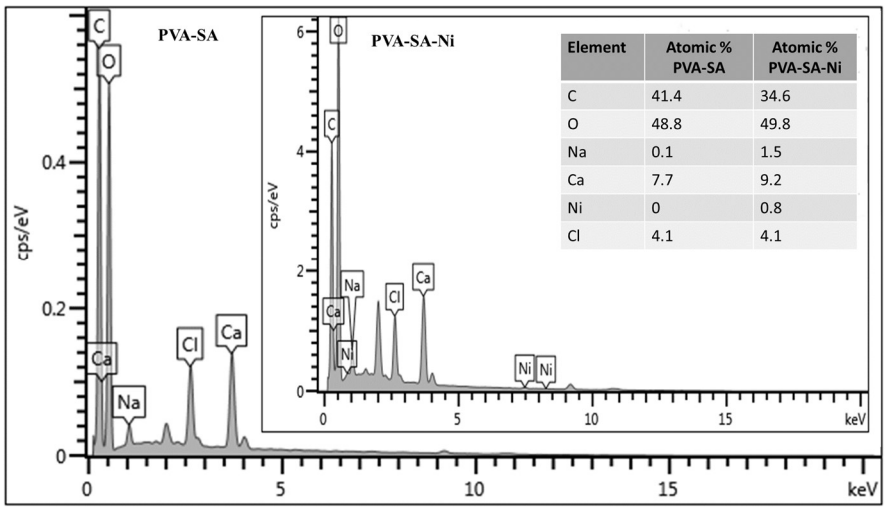


Figure 3. FESEM micrograph of PVA-SA (**A1** and **A2**), PVA-SA-Ni (**B1** and **B2**) and elemental mapping of Ni for PVA-SA-Ni (**C1** and **C2**)



Element	Atomic % PVA-SA	Atomic % PVA-SA-Ni
C	41.4	34.6
O	48.8	49.8
Na	0.1	1.5
Ca	7.7	9.2
Ni	0	0.8
Cl	4.1	4.1

Figure 4. The EDX images of PVA-SA and PVA-SA-Ni

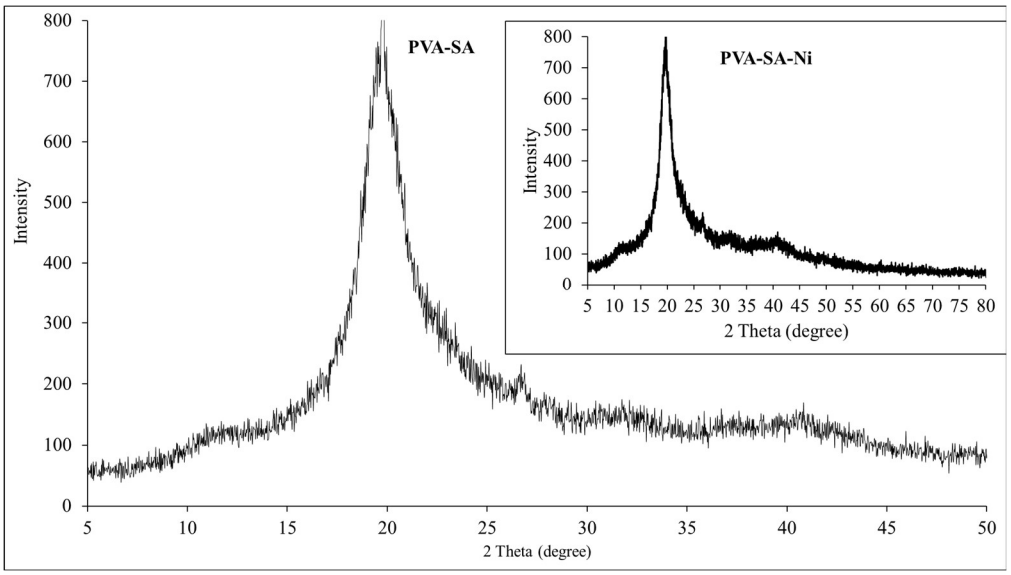


Figure 5. The diffractogram of PVA-SA and PVA-SA-Ni

The first 1 h of reaction, only 36% (Entry 1) of conversion rate was obtained. In order to confirm the substrates have sufficient time to convert to product, the reaction time was increased (Entries 2-5) [21]. Within 4 h of reaction times, 74% (Entry 4) of conversion rate was recorded. However, reaction time increase to 5 h showed no significant changes in conversion rate percentage because deactivation of catalyst caused by the reaction was too long [22]. Thus, 4 h was selected as optimum reaction time for future study in effect of bases, and solvents.

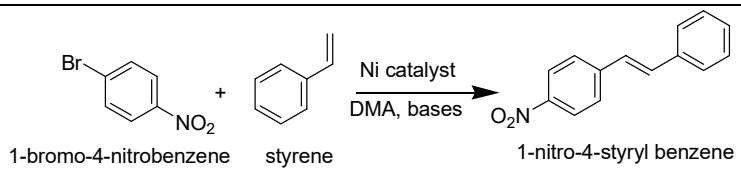
Catalytic activities also would increase by the presence of suitable bases. The function of base is to regenerate active complexes of catalyst by removing hydrogen halide from inactive catalyst complex [23]. In this study, K_2CO_3, Na_2CO_3 and NaOAc (Entries 4, 6-7) were used. The highest conversion rate percentage by using K_2CO_3 probably due to the solubility of base in solvent [21].

The effect of solvent in the catalytic activity has been studied by employing polar solvent DMA, 6.5 (Entry 4) and methanol, 6.1 (Entry 8) and non-polar solvent toluene (Entry 9). Based on Table 2, DMA was the most efficient solvent due to its higher basicity and nucleophilicity [24] as compared to methanol that is less polar. Toluene is not suitable in this catalytic activity due to its non-polar solvent.

From all the results obtained, used of 1 mmol% PVA-SA-Ni catalyst load gained the highest catalytic activity when K_2CO_3 acted as base, DMA as solvent, with temperature at 165 °C and time within 4 h were employed (Entry 4).

The parameter for entry 4 was used to pursue the recyclability study of PVA-SA-Ni catalyst. It is important to evaluate the ease separation of catalyst from reaction mixture. The catalyst was separated from reaction mixture by easy filtration step, wash, dried and used for next catalytic cycle. The reusability of PVA-SA-Ni was three times based on Entry 4, 10 and 11. In the 1st run, the conversion rate of the product was 74%. For the 2nd run, the conversion rate of product was 69%. However, for the 3rd run, the conversion rate obtained was 24% and the catalyst was denatured. The reusability of the heterogeneous catalyst was low maybe due to Ni leaching from FAAS analysis (59%). It is expected that this results in a loss of catalytic because in many cases showed low reusability and low catalytic activity due to the leaching [15].

Table 2. Optimisation of Heck cross-coupling reaction of PVA-SA-Ni (II) catalyst



Entry	Base	Solvent	Time (h)	%Conversion
1	K_2CO_3	DMA	1	36
2	K_2CO_3	DMA	2	40
3	K_2CO_3	DMA	3	51
4	K_2CO_3	DMA	4	74
5	K_2CO_3	DMA	5	69
6	Na_2CO_3	DMA	4	6
7	NaOAc	DMA	4	43
8	K_2CO_3	Methanol	4	2
9	K_2CO_3	Toluene	4	-
10	K_2CO_3	DMA	4	69
11	K_2CO_3	DMA	4	24

*The catalytic study was conducted by using 1 mmol % of PVA-SA-Ni at reflux condition

The plausible reaction mechanisms involved in Heck reaction between 1-bromo-4-nitrobenzene and styrene is shown in Figure 6. The first step is started with the reduction of catalyst, complex $NiCl_2$-A to the catalytic active species Ni(0)-A with the presence of K_2CO_3, where A is PVA-SA polymer. The active species of Ni(0)-catalysed coupling reaction in five steps; (2) oxidative addition of 1-bromo-4-nitrobenzene to generate (a), (3) styrene insertion to form a π-alkene complex (b), (4) migratory insertion to produce σ-alkyl Ni complex (c), (5) rearrangement of the complex by internal rotation to generate (d), β-hydride elimination to release targeted product (e), and the addition of base to regenerate the catalyst by removing hydrogen halide (HX) from the inactive complex.

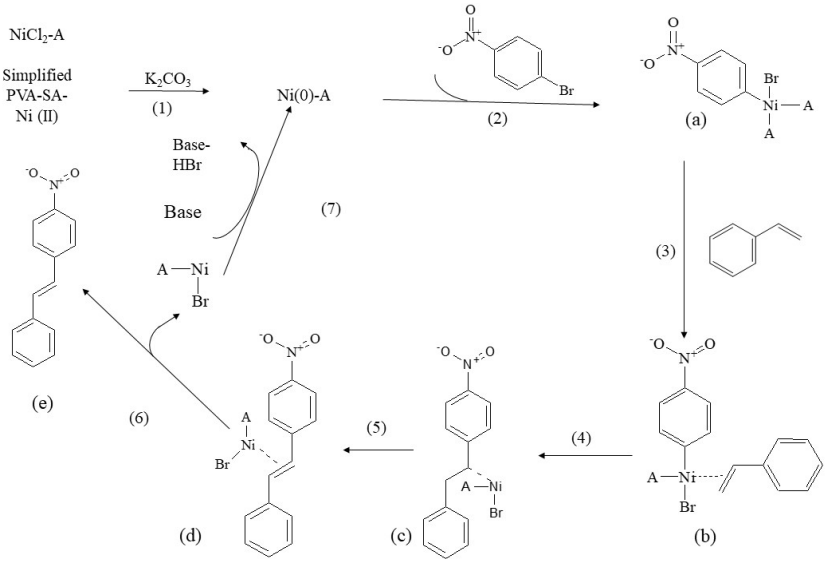


Figure 6. The proposed mechanism of Heck reaction in the presence of a PVA-SA-Ni as a catalyst

Conclusion

This study was successful in supporting $NiCl_2$ by using PVA-SA that form PVA-SA-Ni catalyst utilizing one pot ultrasonic method. The Ni loading in PVA-SA-Ni was 0.14615 % in 50 mg of catalyst. The successful synthesis PVA-SA-Ni was confirmed by using FAAS, ATR-FTIR, FESEM-EDX and XRD. The catalytic activity of catalyst in Heck reaction between 1-bromo-4-nitrobenzene and styrene was analyzed by using GC-FID gave 74% conversion rate at optimum condition. The optimum condition involved K_2CO_3 as base in DMA solvent at 165 °C and 4 h reaction time. The recyclability of catalyst is up to 3 cycles. Therefore, this study produced a novel green technique in preparing Ni catalyst that has potential for Heck reaction. However, study on the structure of catalysts improvement is needed by modification of parameter during synthesis to achieve high metal loading that influence conversion rate percentage and recyclability of catalyst. Further research on optimization of the synthesis parameters and exploring additional factors could potentially enhance the catalytic performance even more. Continuous improvement and refinement of the synthesis process are essential to maximize the efficiency and applicability of the catalyst.

Acknowledgement

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