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Title: Electrochemical Evaluation of Catalytic Activity of Various Types of LDH/Mo<sub>10</sub>V<sub>2</sub>-Pd: Application of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd as an Efficient and Reusable Nano Catalyst in the Heck Coupling Reactions



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PII:	\$0013-4686(17)31905-9
DOI:	http://dx.doi.org/10.1016/j.electacta.2017.09.035
Reference:	EA 30234
To appear in:	Electrochimica Acta
Received date:	30-5-2017
Revised date:	26-7-2017
Accepted date:	6-9-2017

Please cite this article as: {http://dx.doi.org/

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# Electrochemical Evaluation of Catalytic Activity of Various Types of LDH/Mo<sub>10</sub>V<sub>2</sub>-Pd: Application of

FeNi/Mo10V2-Pd as an Efficient and Reusable Nano Catalyst in the Heck Coupling Reactions

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#### Abstract

Palladium nano particles deposited on various forms of layered double hydroxide intercalated 10-molybdovanado phosphate (M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd) were synthesized. Their electrocatalytic behavior and collaboration of all components of synthesized catalysts were evaluated in Heck coupling reaction. According to the obtained results from electrochemical and catalytic investigations, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was chosen as the best in term of productivity. The structural features of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd were characterized by SEM, EDX, TEM, FT-IR, XRD, ICP-AES, LSV, chronoamperometry and CV analyses. The presence of  $Mo_{10}V_2$  improved the catalytic activity of FeNi-Pd in the Heck coupling reaction. Also collaboration of Pd and  $Mo_{10}V_2$  with FeNi LDH as a support was studied. This reusable solid catalyst exhibited excellent activity and the methodology is applicable to diverse substrates providing good to excellent yields of desired products. This method has advantages of high yields, low reaction times, elimination of ligand and base, heterogeneous reusable catalysts and simple methodology.

Keywords: Layered double hydroxide; ; ; ; , Polyoxometalate, Palladium, Cyclic voltammetry, Linear sweep voltammetry.

#### 1. Introduction

Recently, layered double hydroxides (LDH) intercalated by POM have attracted a lot of attention as a potentially important class of materials [1-3]. The general formula for LDH is  $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_{2}]^{x+}A^{n-}_{x/n}.mH_{2}O$ , in which divalent cations are partially substituted for trivalent ones. The layers have positive charges that are balanced by the interlayer anions. The most unique characteristics of LDH are their anion exchange features so that a wide variety of interlamellar anions can exchange with other anions which are in LDH structures [4].

Polyoxometalates (POM) are a unique class of molecular metal-oxygen clusters which have remarkable behaviors in various fields including catalysis, electrocatalysis, medicine and material sciences [5-7]. Most POMs are structures constituted of early transition-metal elements in their highest oxidation states. Their anionic forms, due to their electron and proton transfer and/or storage abilities, can be an efficient donors or acceptors of several electrons without any changes in their structural features. This charge transfer ability makes POMs as ideal candidates for electron exchange reactions. Their redox behaviors depend on their structure and other components which are in contact with them. POMs are reported to adsorb in or on various solid materials and this property has recently been exploited for study on the collaboration comport of POM and these solid materials [8-14].

Exchange of interlayer anions with POMs to prepare POM-LDH intercalates is very important because the products find unusual properties which make them ideal options in various field of science specially in catalyst

industry. These interesting materials have properties of both POM anions and LDH and can present amazing properties as efficient catalysts in many organic reactions.

One of the most important fields of organic transformations is cross coupling reactions which are generally considered to be homogeneous reaction most commonly catalyzed by soluble Pd (II) species with a variety of ligands, such as palladium-phosphine complexes [15], oxime palladacycles [16], palladium-salen complexes [17], or palladium-N-heterocyclic carbine complexes [18]. However, separation of the expensive catalyst from the product for reusing is often problematic in these homogeneous systems. Moreover, aggregation and precipitation of palladium metal in the homogeneous systems always leads to lost activity of the catalysts. Thus heterogeneous catalysts are highly desirable, especially in large-scale synthesis, from both environmental and economic aspects. Much efforts has been paid to developing heterogeneous catalytic systems that can be efficiently reused [19].

Today, growing studies have been performed on the use of POMs in the cross coupling reactions [9, 20, 21]. The electronic structure of Pd is one of the main factors that influences on the catalytic activity of Pd catalysts in the coupling reactions [22-25]. The oxidative addition and reductive elimination steps of coupling cycles are intensively impressed by the electrocatalytic properties of Pd catalyst. Therefore, the presence of species that affects the electronic properties of Pd can change the electrocatalytic properties of Pd and its efficiency in the coupling reaction. Because of the electron transfer ability of POMs [26-28], these compounds can act as efficient donors or acceptors of several electrons to/from Pd species [29]. Such reversible charge transfer ability of POMs with Pd, cause influence on the catalytic activity of the Pd in the coupling reactions. The unique results for coupling reactions catalyzed by palladium and POM systems encourage us to investigate the collaboration of the systems composed of Pd and POM species.

In order to develop a green and efficient protocol based on the use of POMs in organic synthesis [11-14] and emanating from the interest in Pd catalyzed cross-coupling reactions [14, 30, 31] the present study evaluates the catalytic activity and electrochemical behavior of M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd in Heck coupling reaction. In this system, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd shows the best catalytic activity. A low amount of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is used as an efficient catalyst, which reduces costs because of recyclability and increase efficiency in Heck reaction.

#### 2. Experimental Section

#### 2.1. General remarks

All of the reagents were commercially available and purchased from Merck, Fluka, and Aldrich chemical companies. Transmission electron microscopy (TEM) analyse was investigated using a TEM microscope Philips CM 120 KV Netherland. Scanning electron diffraction microscopy (SEM) was performed using an SU3500 microscope

with scanning range from 0 to 20 keV. Electron dispersive X-ray spectroscopy (EDX) measurements were made with an IXRF model 550i attached to SEM. SEM/EDX samples were prepared by coating of solid particles into a conductive layer. X-ray diffraction (XRD) patterns were recorded on Inel French, EQUINOX 3000 model X-ray diffractometer using Cu-K radiation. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded with KBr pellets using a Bruker ALPHA FT-IR spectrometer. The Pd and Mo contents were evaluated using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD spectrometer. The electrochemical behaviors of the catalyst were measured using computer controlled m-Autolab modular electrochemical system (SAMA500 ElectroAnalyzer system). Thin layer chromatography (TLC) on precoated silica gel Fluorescent 254 nm (0.2 mm) on aluminum plates was used for monitoring the reactions. The cross coupling products were characterized by their <sup>1</sup>H NMR spectra.

#### 2.2. Preparation of M(III)M(II) LDH

To prepare M(III)M(II) LDH, an aqueous solution of NaOH and Na<sub>2</sub>CO<sub>3</sub> (100 ml alkaline solution, 0.32 g Na<sub>2</sub>CO<sub>3</sub>, 0.48 g NaOH)) was slightly added to a mixture of M(III) and M(II) metal nitrate aqueous solution  $(M(II)/M(III) = 3.0 \text{ mol mol}^{-1})$  at 70°C under vigorous stirring and N<sub>2</sub> atmosphere. The addition of alkaline solution was continued until the solution pH was adjusted to 10.0. The resulting material was then aged at 90°C for 12 h. The obtained precipitate was cooled to room temperature and separated by filtration, then washed with distilled water several times and dried at 100°C for 24 h.

#### 2.3. Preparation of M(III)M(II)-Pd

In order to prepare M(III)M(II)-Pd, 255 ml PdCl<sub>2</sub> aqueous solution (0.008 M) was prepared. Then 0.5 g M(III)M(II) LDH was added into mentioned solution and its pH was adjusted to 10.0 by addition of 0.1 M NaOH. The solution was heated to 80°C in water bath under stirring for 1 h. The resulting slurry was separated, followed by washing with deionized water until no Cl<sup>-</sup> remained and dried at 60°C for 24 h to produce M(III)M(II)-Pd.

#### 2.4. Preparation of M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd

The anion exchange reactions with  $[PMo_{10}V_2O_{40}]^{5-}$   $(Mo_{10}V_2)$  anions were done with addition of 50 mL of  $Mo_{10}V_2$  solution (0.0035 M) to a suspension of M(III)M(II)-Pd (1.00 g) under N<sub>2</sub> atmosphere. The mixture was kept under N<sub>2</sub> and refluxed in the temperature range of 90-95°C for 10 h. The resulting solid was filtered and washed with boiling water three times, and then dried in vacuum.

#### 2.5. Electrode Preparation

LDH based structure modified carbon paste electrodes (CPE) were fabricated by mixing powder graphite, LDH based structure, and paraffin oil thoroughly until a paste was obtained. The resulting paste was loaded into the tip of a micropipette (4 cm long, 0.01 cm diameter) with Cu wire serving as an electrical connection. Each time an experiment was performed, the electrode was refreshed by forcing out the used paste, loading a fresh paste and smoothening the surface by polishing on a weighing paper. To investigate electrochemical features of synthesized catalysts, the prepared electrode was inserted in three electrodes chemical cell composed of saturated calomel electrode (SCE) and platinum counter electrode.

#### 2.6. General procedure for the Heck coupling reaction

In a typical procedure, a reaction vessel was charged with aryl halide (4.0 mmol), styrene (4.0 mmol), tetrabutylammonium bromide, TBAB (4 mmol), 0.02 g of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd (mmol Pd/mmol Substrate: 0.0035) and 5 mL dimethyl formamide (DMF). The resulting mixture was refluxed at 120°C under dry nitrogen atmosphere for appropriate time. Progress of the reaction was monitored by TLC. Upon completion of the reaction, the solution was allowed to cool, and catalyst was separated by centrifuging, washed with diethyl ether (2×10 mL), water (2×10 mL), and then dried under vacuum for reusing. The residual mixture was extracted with diethyl ether and the organic phase separated. The solvent was evaporated and the crude products were characterized by <sup>1</sup>H NMR spectroscopy.

#### 3. Results and Discussion

A series of  $M(III)M(II)/Mo_{10}V_2$ -Pd was synthesized and used as nano catalyst for the Heck coupling reaction under base and ligand free conditions.

The synthetic route for the synthesis of the designed heterogeneous catalysts is presented in Scheme 1. The  $M(III)M(II)/Mo_{10}V_2$ -Pd was synthesized by using a method that comprise the separated synthesis of M(III)M(II) LDH, deposition of Pd nano particles on M(III)M(II) LDH and intercalation of  $Mo_{10}V_2$  in M(III)M(II)-Pd structure.

A series of catalysts including FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlCo/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlZn/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeZn/Mo<sub>10</sub>V<sub>2</sub>-Pd and FeNiPd/Mo<sub>10</sub>V<sub>2</sub> was applied to the transformation of bromobenzene and styrene into corresponding product (Scheme 2 and Table 1).

According to the obtained results from Table 1, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd (entry 1) can catalyze the Heck reaction efficiently and the corresponding product was obtained in excellent yield at short reaction time. To compass the reason of better performance of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd compare with other catalysts and relationship between LDH, Pd and Mo<sub>10</sub>V<sub>2</sub> species in the Heck coupling reactions the electrochemical behavior of aforementioned catalysts were investigated.

The linear sweep voltammetry (LSV) curves in Fig. 1a confirm the electrocatalytic performance of series of synthesized LDHs. As shown in Fig. 1a, the onset overpotential of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is 0.155 V while it is 0.163, 0.167, 0.169, 0.174 and 0.178 V for AlCo/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlZn/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeZn/Mo<sub>10</sub>V<sub>2</sub>-Pd and FeNiPd/Mo<sub>10</sub>V<sub>2</sub> respectively. The current density at 0.19 V for FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is 23.94 mA, which is higher than that for other catalysts. In comparison to FeNi-Pd and FeNi LDH, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd delivers substantially higher electrocatalytic activity showing that the synergistic effect of Mo<sub>10</sub>V<sub>2</sub>, FeNi LDH and Pd species which can greatly improve the electrocatalytic activity of Pd (Fig. 1b). As resulted from Fig. 1b, the onset overpotential of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd negatively shifts to lower potentials, which is significantly smaller than FeNi-Pd and FeNi LDHs. Thus, the presence of Mo<sub>10</sub>V<sub>2</sub> in the FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd structure cause improves the electrocatalytic activity of the catalyst in terms of both the onset overpotential and current density, highlighting the importance of the presence of Mo<sub>10</sub>V<sub>2</sub> in catalyst structure.

The Tafel slope is often used as a primary activity parameter in determining the catalytic activity. A catalyst with a high charge transfer ability should possess a low Tafel slope value [32]. As shown in Fig 1c, the low Tafel slope of 15 mV dec<sup>-1</sup> obtained for FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd catalyst. Obviously, the Tafel slope for FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd catalyst is smaller than other slopes which means that more facile electron transfer through the layer of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd catalyst was occurred.

To understand the reason behind the variation of catalytic performance of LDH based catalysts in Heck coupling reaction, electrochemical active surface areas (ECSA) of synthesized catalysts were investigated using cyclic voltammetry (CV) in pH=5 of 0.1 M phosphate buffer solution (PBS). In order to evaluate the ECSA of a series of the synthesized catalysts, the attributed palladium redox peaks as a main catalyst were used. The typical CV curves of the catalysts with different scan rates are presented in Fig. 2. By plotting the  $\Delta J=(J_c-J_a)$  which corresponded to catalysts versus SCE against the scan rate, the linear slope can be used to represent the attributed ECSA [33-35]. ECSA is a very important factor for catalysts in electrochemical reactions, as it is well known that an increase of active surface area often leads to enhancement of the catalytic activity.

ECSA of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is 0.0628 mA cm<sup>-2</sup>, while other catalysts have a lower linear slope which means FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd has a more electroactive surface than others (Fig. 2). This can contribute to enhancement of catalytic activity of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd in Heck coupling reactions presented in Table 1.

Also, in order to investigate the effect of  $Mo_{10}V_2$  on the catalytic activity of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, the electrocatalytic behaviors of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and FeNi-Pd were investigated in 0.1 M pH=5.0 PBS by CV (Fig. 3). The cyclic

voltammogram of FeNi LDH shows the redox current peaks in the potential range of 0.05 to 0.3 V, which correspond to the reversible reactions of Ni(II)/Ni(III or IV) for all the LDH samples [36]. After deposition of Pd nanoparticles on the surface of FeNi LDH, in the potential range of 0.1 to 0.4 V, the Pd(0)/Pd(II) redox waves are well-separated from FeNi LDH redox waves in -0.02 to 0.1 V. After intercalation of  $Mo_{10}V_2$  in the catalyst, three pairs of redox peaks were observed for FeNi/ $Mo_{10}V_2$ -Pd modified electrode. It can be attributed to electron-transfer reaction of Mo(V)/Mo(IV), Mo(IV)/Mo(III), and V(V)/V(IV) couples.  $Mo_{10}V_2$  with reversible charge transfer ability to/from Pd species cause influence on the catalytic activity of the Pd. The obtained results from the comparison of cyclic curves of FeNi/ $Mo_{10}V_2$ -Pd and FeNi-Pd demonstrated that the presence of  $Mo_{10}V_2$  not only enhanced the oxidation peak current of FeNi-Pd but also decreased its oxidation peak potential from 0.34 to 0.25 V, suggesting that the electrochemical oxidation strength of FeNi-Pd was facilitated by presence of  $Mo_{10}V_2$ . The reproducibility of differences was tested by consecutive scans at constant conditions. The RSD for all differences was evaluated below 6.0%. These results demonstrate that all of the measurements are nearly identical with constant response, indicating that the amount of differences has extraordinary reproducibility.

The FT-IR spectra of FeNi LDH,  $Mo_{10}V_2$ , FeNi/ $Mo_{10}V_2$ -Pd and recovered FeNi/ $Mo_{10}V_2$ -Pd illustrated in Fig. 4. The absorption bands at 527 and 689 cm<sup>-1</sup> attributed to the M-O vibration modes of LDH structure (curve a). The infrared band around 1618 cm<sup>-1</sup> can be attributed to the hydroxyl deformation mode of the interlayer water molecules. Also, the characteristic absorption around 1386 cm<sup>-1</sup>, corresponding to intercalated  $CO_3^{2-}$  was observed. The existence of  $Mo_{10}V_2$  in the catalyst structure was investigated by presentation of FT-IR spectrum of the  $Mo_{10}V_2$  (curve b). The bands for the Keggin structure of neat  $Mo_{10}V_2$  occurred at 1168, 1021, 927 and 814 cm<sup>-1</sup>. FT-IR spectra of FeNi/ $Mo_{10}V_2$ -Pd in addition of FeNi LDH peaks at 522 and 684 cm<sup>-1</sup>, shows the presence of Keggin-type structure at 1161, 1016, 911 and 801 cm<sup>-1</sup> which is in agreement with the results reported previously (curve c) [14]. It is notable that, the peaks at about 1386 cm<sup>-1</sup> which confirm the presence of carbonates in LDH structure disappeared in the FeNi/ $Mo_{10}V_2$ -Pd sample, suggesting that the anion exchange was complete.

In XRD pattern of FeNi LDH, reflexion peaks at 20 of 11.2, 22.1, 33.9, 38.7, 46.02, 59.3 and 60.01° can be indexed to (003), (006), (009), (015), (018), (110) and (113) facets of LDH which are characteristics of FeNi LDH (Fig. 5. pattern a) [37]. The presence of  $Mo_{10}V_2$  in the catalyst structure was confirmed by presentation of XRD pattern of the  $Mo_{10}V_2$  (pattern b). After pillaring of  $Mo_{10}V_2$  into the LDH structure, the reflexion pattern of the FeNi/ $Mo_{10}V_2$ -Pd (pattern c) shows a characteristic band of LDH layer in addition of  $Mo_{10}V_2$  reflexions. Moreover, pattern c, after the Pd immobilization processes indicates the presence of Pd nano particles on the layers of LDH. Pd(0) nano particles

in the catalyst have crystalline structure with peak appearing at 67.92° attributed to the (220) planes of Pd crystalline structure {JCPDS-05-0681}.

The structure morphology of the fabricated FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was characterized by SEM-EDX analyses (Fig. 6). SEM images show that the fresh FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd has well developed with layered structures (Fig. 6a-c, e). The SEM images of the catalyst demonstrated that, Pd nano particles are deposited on layers of the catalyst. Also the EDX mapping analysis of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is shown in Fig. 6f-i, which indicated that the Pd nano particles are deposited on the surface of the FeNi LDH structure and Mo<sub>10</sub>V<sub>2</sub> are homogeneously distributed throughout the layers of LDH structure. Elementary analysis of the surface is further studied by using EDX. EDX pattern of the FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is shown in Fig. 6k. EDX pattern of the catalyst shows major peaks of Ni, Fe, Mo and V. These results confirm the presence of FeNi LDH, Mo<sub>10</sub>V<sub>2</sub> and Pd nano particles on the surface of the synthesized catalyst.

The amount of Pd content on the surface of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd as a main catalyst was 7.49 wt%, which was determined using ICP-AES measurement. Also according to the obtained results from ICP-AES measurement the content of Mo was 7.19 23.64 wt% indicated that the amount of  $Mo_{10}V_2$  in FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd structure was 42.81 wt%.

The detailed morphology and structure of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd were further studied using TEM, as shown in Fig. 7. The TEM images of catalyst show the characteristic thin nano sheet of FeNi LDH structure. In addition, the TEM investigations indicated that the Pd nano particles were deposited on the surface of LDH nano sheets with nanometer size range smaller than 40 nm.

In the Heck coupling reaction a variety of parameters, such as catalyst amount and solvent can influence on the reactivity of the reactions. In this study, the FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was investigated as catalyst in the model Heck coupling reaction of bromobenzene, and styrene (Scheme 2). So, initially, the reaction was performed in the presence of various solvents, such as H<sub>2</sub>O, dimethyl acetamid (DMAc), dimethyl formamide (DMF) and mixture of DMF and H<sub>2</sub>O. (Table 2, entries 1-4). DMF at 120°C is the best choose in terms of yield and reaction time (entry 1).

It is notable that, the presence of TBAB in the Heck reaction is necessary. One of the most effective ways to increase the Heck reaction yield is applying the Jeffery conditions, *i.e.* introduction of TBAB to the reaction medium [38]. In the Heck coupling reaction TBAB can act as stabilizers of Pd colloids, preventing their aggregation to the bigger size particles, usually inactive or less active [39, 40]. Also the TBAB can role as phase-transfer agents in this coupling reaction [38, 41, 42].

One of the most important factors that affected on catalysts efficiency in electrochemical reactions is their electrostability. As expected, the current density of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is larger than other catalysts. In addition, the slop

of current decadence for FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd is lower than that for other LDH based catalysts (Fig. 8a). These results indicated that FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd has better electrochemical catalytic activity and stability. As shown in Fig. 8b, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd exhibited a slower current decay over time than the FeNi-Pd and FeNi LDH. It is notable that the presence of  $Mo_{10}V_2$  in catalyst structure, significantly improves its electrocatalytic activity, as well as stability.

Next, different amounts of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, were employed to improve the productivity of the reaction. An excellent yield was found with 0.02 g of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd (Table 2, entry 1) at 120°C after 9 h. Using less amount of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd led to lower yield and further increasing in the catalyst quantity showed no improvement on the reaction time and yield (Table 2, entries 5, 6).

One of the purposes for designing this heterogeneous system is the ability of recycling of the catalyst for reusing in subsequent reaction runs. To study the recyclability of the catalyst, the reaction of bromobenzene with styrene as a model reaction in the presence of 0.02 g FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was used. After the completion of the reaction, the mixture from the first-run reaction was centrifuged, and the obtained solid was washed alternately with suitable solvent. After drying, the recovered catalyst was then reused in the same reaction under identical conditions. The catalyst revealed a remarkable activity and was reused up to at least four consecutive cycles without any significant decrease in the catalytic activity of the catalyst. At the fourth reaction runs, the yield of the product decreased from 89 to 78% after fourth runs.

The structural changes of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd after the reaction process were studied using FT-IR, XRD and SEM techniques. The obtained results demonstrated that the structure of the catalyst was retained unchanged after the reaction cycle and reusing process (Fig. 4d, Fig. 5d and Fig. 6d).

#### 4. Conclusion

The present study reported the synthesis and utilization of a series of LDH based catalysts including FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlCo/Mo<sub>10</sub>V<sub>2</sub>-Pd, AlZn/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeZn/Mo<sub>10</sub>V<sub>2</sub>-Pd and FeNiPd/Mo<sub>10</sub>V<sub>2</sub> in the Heck coupling reaction. Among aforementioned catalysts, FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd seems more efficient than others in Heck coupling reaction. The presence of  $Mo_{10}V_2$  in the catalyst structure is essential for obtaining high performances of the catalyst; most probably it can activate precursors of the reaction and transfer the electron to Pd species that facilitate the regeneration of Pd species in the reductive elimination step. The structure of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was characterized by FT-IR, XRD, ICP-AES, TEM, SEM, EDX, CV, LSV and chronoamperometry analyses techniques. Of significant practical importance are the findings of excellent activity and the ability to readily recover and reuse the catalyst with no apparent loss of activity.

#### Acknowledgment

The authors thank the Razi University Research Council and Iran National Science Foundation (INSF) for support of this work.

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Entry	Catalyst	Time (h)	Yield (%) <sup>b</sup>
1	FeNi/Mo <sub>10</sub> V <sub>2</sub> -Pd	9	89
2	AlCo/Mo <sub>10</sub> V <sub>2</sub> -Pd	12	71
3	FeZn/Mo <sub>10</sub> V <sub>2</sub> -Pd	24	42
4	AlNi-Mo <sub>10</sub> V <sub>2</sub> -Pd	24	58
5	AlZn/Mo <sub>10</sub> V <sub>2</sub> -Pd	24	49
6	FeNiPd/Mo <sub>10</sub> V <sub>2</sub>	24	17

<b>Table</b>	1. Heck	coupling	reaction	in the	presence	of variou	s catalysts <sup>a</sup> .
		1 0			1		2

<sup>a</sup>Reaction conditions: Styrene (4 mmol), bromobenzene (4 mmol), TBAB (4 mmol), DMF (5 mL) under N<sub>2</sub> atmosphere

at 120°C.

<sup>b</sup>Isolated yield.

Entry	Amount of the Catalyst (g)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	0.02	DMF	9	89
2°	0.02	$H_2O$	24	24
3	0.02	DMAc	24	62
4	0.02	DMF/H <sub>2</sub> O (5:1)	12	71
5	0.01	DMF	12	68
6	0.03	DMF	9	91

Table 2. O	ptimization of	f Heck couplii	ng reaction	conditions. <sup>a</sup>

<sup>a</sup>Reaction conditions: styrene (4 mmol), bromobenzene (4 mmol), TBAB (4 mmol) under  $N_2$  atmosphere at 120°C.

<sup>b</sup>Isolated yield.

<sup>c</sup>The reaction was proceeded in the reflux condition.

Entry	Aryl halide	Time (h)	Yield (%) <sup>b</sup>
1	Br	9	89
2	O <sub>2</sub> N Br	8	94
3	OHC	8	88
4	Br	14	73
5	H <sub>3</sub> C Br	12	76
б	H <sub>2</sub> N Br	14	64
7	Br	14	76
8	Br	14	86
9	CI	24	56

<b>Table 3.</b> Heck reaction of various arvl halides with styrene. <sup>a</sup>	reaction of various arvl halides with styrene. <sup>a</sup>
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 $\label{eq:aReaction conditions: styrene (4 mmol), bromobenzene (4 mmol), TBAB (4 mmol), DMF (5 mL) under N_2 atmosphere$ 

at 120°C.

<sup>b</sup>Isolated yield.

#### **Figure Captions**

**Fig. 1**. LSV curves of a) a series of synthesized M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd, b) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeNi-Pd and FeNi LDH, 40 mV/S.

Fig. 2. Typical CV curves of M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd carbon paste electrode in pH=5 of PBS with different scan

rates and their  $\Delta J (= J_c - J_a)$  plotted against scan rates.

Fig. 3. CV curves of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and FeNi-Pd carbon paste electrode in pH=5 of PBS, 40 mV/S.

Fig. 4. FT-IR spectra of a) FeNi LDH, b) Mo<sub>10</sub>V<sub>2</sub>, c) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and d) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.

Fig. 5. XRD patterns of a) FeNi LDH, b) Mo<sub>10</sub>V<sub>2</sub>, c) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and d) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.

Fig. 6. SEM images of a, c) fresh FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, b) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, d-g) mapping results of

FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd h) EDX images and i) elemental analysis of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.

Fig. 7. The TEM images of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.

Fig. 8. Chronoamperometry curves at 0.19 V vs. SCE of a) a series of synthesized M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd and b)

FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeNi-Pd and FeNi LDH.

Fig. 9. Reusability of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd in the model reaction.

Scheme 1. Synthetic route of M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd.

Scheme 2. Reaction of styrene and bromobenzene as a model reaction.



Fig. 1. LSV curves of a) a series of synthesized  $M(III)M(II)/Mo_{10}V_2$ -Pd, b) FeNi/Mo<sub>10</sub>V\_2-Pd, FeNi-Pd and FeNi LDH, 40 mV/s, c) Tafel plots of synthesized  $M(III)M(II)/Mo_{10}V_2$ -Pd, all of the measurements were performed in 0.1 M PBS.



**Fig. 2.** Typical CV curves of M(III)M(II)/Mo<sub>10</sub>V<sub>2</sub>-Pd carbon paste electrode in pH=5 of PBS with different scan rates and their  $\Delta J$  (= $J_c$ - $J_a$ ) plotted against scan rates.



Fig. 3. CV curves of FeNi LDH, FeNi-Pd and FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd carbon paste electrode in pH=5 of PBS, 40 mV/S.



Fig. 4. FT-IR spectra of a) FeNi LDH, b) Mo<sub>10</sub>V<sub>2</sub>, c) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and d) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.



Fig. 5. XRD patterns of a) FeNi LDH, b) Mo<sub>10</sub>V<sub>2</sub>, c) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and d) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd.



**Fig. 6.** SEM images of a-c, e) fresh FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, d) recovered FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, f-i) mapping results of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, j) elemental analysis of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd and k) EDX image of FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd was performed in 10.0 KV.



Fig. 7. The TEM images of FeNi/Mo $_{10}$ V<sub>2</sub>-Pd.



Fig. 8. Chronoamperometry curves at 0.19 V vs. SCE of a) a series of synthesized  $M(III)M(II)/Mo_{10}V_2$ -Pd and b) FeNi/Mo<sub>10</sub>V<sub>2</sub>-Pd, FeNi-Pd and FeNi LDH.



Fig. 9. Reusability of FeNi/Mo $_{10}$ V<sub>2</sub>-Pd in the model reaction.



Scheme 1. Synthetic route of  $M(III)M(II)/Mo_{10}V_2$ -Pd.



Scheme 2. Reaction of styrene and bromobenzene as a model reaction.

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