



# Heck reaction catalyzed by colloids of delaminated Pd-containing layered double hydroxide

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## ABSTRACT

A novel ligand-free catalyst, Pd(II)-doped colloidal layered double hydroxide (LDH) has been prepared from delamination of glycinate-intercalated ternary-component MgPdAl-LDH ( $[\text{Mg}_{0.95}\text{Pd}_{0.05}\text{Al}_{1/3}(\text{OH})_2][\text{Gly}_{1/3}\cdot m\text{H}_2\text{O}]$ ) in formamide. The catalytic performance of these mono-dispersed ultrathin nanosheets of LDH for Heck reaction was evaluated. Owing to the largely enhanced accessibility for reactant molecules resulting from the nature of high inner surface area of LDHs, these palladium-bearing nanosheets showed excellent efficiency in Heck reactions in a wide range of substrate molecules. The presence of Mg, Al and  $\text{OH}^-$  ions in the LDH-lamellas favors control the size growth of the *in situ* formed Pd(0) species implanted in the LDH layer matrixes, helping to prevent the formed Pd(0) from extraction from the lamellas followed by Pd-black formation. Moreover, the Pd sites and basic sites on the brucite-like nanosheets are combined at a molecular level and interact with each other closely because of the co-precipitation method employed; so the basic sites on the LDH monolayers might function as basic ligands. This new catalyst, delaminated MgPdAl-LDH, was characterized by XRD, TEM, HRTEM and EDX analysis.

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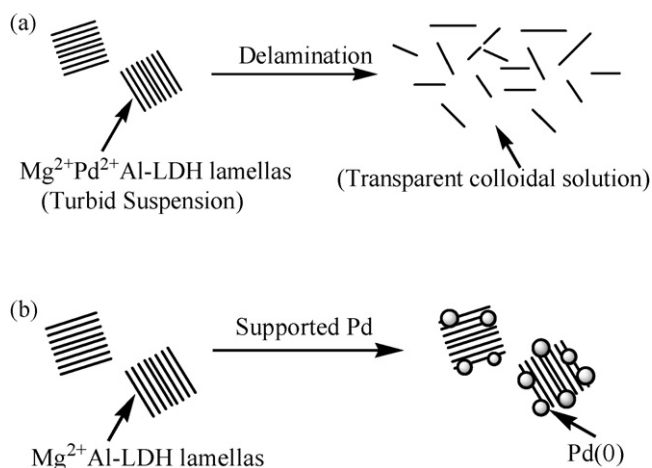
## 1. Introduction

Layered double hydroxides (LDHs), an important family of inorganic-layered materials, have found wide applications as catalysts, catalyst precursors or supports, adsorption, nanocomposite and drug delivery [1–5]. Because of the glue effect of amorphous LDH materials [6], conventionally synthesized LDH are usually heavily aggregated into a secondly particle size of 1–10  $\mu\text{m}$  [7]. There are hundreds of thousands of sheet-like LDH nanocrystallites in each aggregate [8,9]. To take full advantage of LDH materials in catalysis or biomedical applications, it is necessary to disperse LDH aggregates into individual sheet-like nanocrystallites in a stable colloidal solution. Several methods for obtaining colloidal LDH have been developed, including disaggregation of the secondly LDH particles into mono-dispersed LDH nanoparticles through hydrothermal post-treatment to the as-prepared LDHs [8–11], separate nucleation and aging steps (SNAS) [7,12,13] and treatment with certain solvents to delaminate LDH into single lamellas. For instance, the surfactant-intercalated LDH could be delaminated by

non-polar solvents [14–17]. On the other hand, the pristine stacking structure of  $\text{NO}_3^-$  or glycinate ( $\text{Gly}^-$ )-intercalated LDH could also be delaminated into single lamellas (with a thickness of 0.8–1.3 nm) by interaction of certain polar solvents such as derivatives of formamide [18–26]. Delaminating layered materials is of tremendous practical importance in applications due to the largely enhanced accessibility of their inner surface. Layered double hydroxides are layered materials constituted by a stacking of positive hydroxylated layers  $[\text{M}_{1-x}\text{M}_x^{2+}(\text{OH})_2]^{x+}$  separated by interlayered anionic species and water molecules  $[\text{A}_{x/n}^{n-}\cdot m\text{H}_2\text{O}]^{x-}$ . The high charge density of layers make the delamination of LDHs somehow more difficult compared with smectite clay minerals, but the rich chemistry of brucite-like layers will render its delaminated forms more promising as multifunctional materials. For example, catalytically active LDH ultrathin sheet might be obtained from delaminating LDHs that contains active sites. As a consequence of its structure, the delaminated LDH phase would reach a theoretical specific surface area of 1000  $\text{m}^2/\text{g}$ . Actually, applications of delaminated layered materials rather than LDHs have been developed previously [27–31]. However, the practical application of delaminated LDH is still in its infancy, despite that the strategies for delaminations of LDHs have been relatively well-documented and well-established [14–26] since the first case of the LDH delamination by use of surfactant was reported in 2000 [14]. As a newly developed phase of LDH, we anticipate that the catalysis of delaminated or nano-

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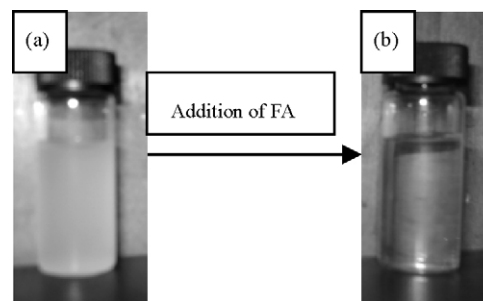


**Scheme 1.** Differences among the conventional MgPdAl-LDH, delaminated MgPdAl-LDH and LDH-supported Pd catalysts.

sized LDHs will be an important trend in the LDH chemistry [32,33].

Palladium is one of the most important catalysis elements in modern organic synthesis [34]. The combinations of Pd and LDH or calcinated derivatives of LDH [35,36] were usually achieved by two representative methods. The first is that incipient wetness impregnation of LDH or its calcined derivatives with the solution containing palladium (Scheme 1b) [37–43]. The second is to introduce palladium directly into the host brucite-like layers through the co-precipitation method to form a ternary-component LDH (the left of Scheme 1a) [44,45], occasionally followed by further calcination [46]. As for the former method, it is not fully reproducible and may give rise to some dishomogeneity of the metal distribution on the surface [47,48]. Although the co-precipitation methods usually lead to a homogeneous distribution of palladium in the brucite-like layers [49], a large fraction of the Pd sites is useless because of the lack of accessibility to the inner surface of LDHs. Both types of catalyst were also reported by us previously, i.e., the catalytically active  $\text{Cu}^{2+}$ -containing LDH [50] and LDH-supported Pd catalyst [39]. The aim of this study is to make a further improvement to the LDH-related catalyst. To make full use of the catalytic sites and lower the catalyst loading, we develop herein a novel catalyst based on delaminated MgPdAl-LDH in which the total surface of catalytic site-bearing compound will be rendered accessible to reactants (the right of Scheme 1a). Scheme 1 expresses the major differences among the bulky MgPdAl-LDH, MgAl-LDH-supported Pd and the delaminated MgPdAl-LDH catalysts. As a new LDH-related Pd catalyst and a newly developed phase of LDH, delaminated LDH differs from the conventional LDH in many respects. If bulky LDH particles were seen as a “books”, the delaminated LDH could be seen as single “leaves”. Compared with the stacking “books”, the area of accessible surface for these mono-dispersed single “leaves” will be largely increased. In our case, the catalytically active sites were incorporated into the single “leaves” rather than supported onto a “book” (i.e., conventional LDH-supported catalyst). Whereas the dispersions of bulky LDH are turbid solid/liquid two-phase system, and the delaminated LDHs are transparent colloidal solutions (Fig. 1). The delaminated LDH could be seen as semi-heterogeneous (or semi-homogeneous) catalytic system.

MgPdAl-LDH single lamellas were obtained herein from the delamination of glycinate-intercalated ternary-component MgPdAl-LDH in formamide according to the reported methods [18,26]. Delaminating LDHs by certain solvents will result in transparent colloidal solutions that is constituted of so-called single



**Fig. 1.** MgPdAl-LDH-Gly was dispersed ultrasonically in DMF (a) and MgPdAl-LDH-Gly dispersed in DMF followed by further addition of FA (b).

LDH-lamellas usually 0.8–1.3 nm in thickness [20,21]. The catalytic aspects of these bifunctional single brucite-like sheets that contain basic sites and Pd sites were investigated subsequently. Owing to the colloidal nature of the dispersion of MgPdAl-LDH ultrathin sheets, a catalyst with high performance for Heck reaction was obtained as expected. The “Heck reaction” [51,52], one of the most powerful C–C bond forming reactions in modern chemistry [53], is usually a Pd-catalyzed C–C coupling between aryl or vinyl halides and triflates with alkenes. As regards to the pre-catalysts of Heck reaction, much attentions have been paid to the ligated Pd, molecular Pd(II), Pd(OH)<sub>2</sub> [54,55] and cluster Pd(0); Pd(II)-doped colloidal nano-sized particles as pre-catalysts are rarely reported however.

## 2. Experimental

The chemicals used were of reagent grade or higher purity. Deionised water was used throughout the experiments. Palladium nitrate was purchased from Shanghai Reagent Co. Ltd. and used without further purification.

### 2.1. Preparation of delaminated MgPdAl-LDH

The starting glycinate-intercalated MgPdAl-LDH with  $(\text{Mg} + \text{Pd})/\text{Al} = 3.0$  (MgPdAl-LDH-Gly) was prepared by co-precipitation. The synthesis was carried out at constant temperature (65 °C) and pH (10.5 ± 0.1) under nitrogen atmosphere. Prior to use, all deionised water was boiled while nitrogen was bubbled through in order to remove carbon dioxide. All sodium hydroxide used was pre-treated with Ba(OH)<sub>2</sub> to remove the unavoidable carbonate. During synthesis two aqueous solutions A and B (A: 30 mL solution containing 2.5 mmol Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, 47.5 mmol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 16.7 mmol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O; B: 50 mL 3 M pre-treated NaOH) were added to the vigorously stirred mother solution (initially containing 100 mL 3 M H<sub>2</sub>NCH<sub>2</sub>COO<sup>−</sup>, balanced by Na<sup>+</sup>) at constant pH and temperature in a water bath. Reactant A was added at a constant flow of 0.5 mL min<sup>−1</sup>, while the basic solution B was added under control to ensure a constant pH (pH meter). During the reaction process, light brown slurry was formed because of the presence of Pd<sup>2+</sup>. To ensure a homogeneous distribution of the M(II) and M(III) cations within the brucite-like layers, strict pH control is needed. The reaction was carried out in a nitrogen atmosphere to avoid adsorption of CO<sub>2</sub>. For the purpose of getting a well-crystallized LDH, the mixture was further aged at 65 °C for 5 h after the completion of the reaction. Then the precipitated product was separated from the solution by centrifugation and washed several times by repeated centrifuging and replacement of the CO<sub>2</sub>-free washing water in sealed containers to remove ions as completely as possible. Because the presence of water in LDH favors delamination actions [18], the wet LDH after washing was just dried gently at room temperature under nitrogen

flow. The resulting light brown solid was designated as MgPdAl-LDH-Gly. In the present work we obtained totally 10 g gently dried MgPdAl-LDH-Gly, which was stored in an air-tight container for further delamination. Delamination of MgPdAl-LDH-Gly were carried out in *N,N*-dimethylformamide (DMF), formamide (FA) and the mixture of FA and DMF (with molar ratio of 1:1), respectively. Dispersions of MgPdAl-LDH-Gly in these solvents were prepared at concentrations of 1 g/L. To facilitate the exfoliation, an ultrasonic or shaking treatment to these dispersions was necessary.

## 2.2. Instruments employed

The X-ray diffraction (XRD) was performed using a Rigaku D/max-rA rotating anode X-ray diffract meter equipped with a Cu K $\alpha$  tube and Ni filter ( $\lambda = 0.1542$  nm). The scan speed was 3°/min at 40 kV and 30 mA. Transmission electron microscopy (TEM) images were obtained by a JEM-200CX transmission electron microscope with an accelerating voltage of 160 kV. High-resolution TEM (HRTEM) observations and energy-disperse X-ray spectroscopy were performed on a JEM-2010HR (JEOL) electron microscope operated at 200 kV and equipped with an energy-disperse X-ray spectrometer. Because of high boiling point of solvents, sample-supported copper grids were vacuum dried at 80 °C for 4 h before TEM observations.

All NMR spectra were recorded on Bruker Avance Digital (400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR) spectrometers; chemical shifts are expressed in  $\delta$  units relative to TMS signal as internal reference. Mass spectra were recorded on a HP5989B mass spectrometers.

## 2.3. Optimization of reaction conditions for the Heck reaction

To evaluate catalytic activity of different exfoliated MgPdAl-LDH-Gly toward Heck reaction, we chose three-solvent systems for the purpose of comparison, they were DMF, FA and the mixture of DMF and FA. A typical procedure was as follows: 10 mmol of bromobenzene, 12 mmol of styrene, 15 mmol of NaOAc, 0.5 mL of water and 10 mL dispersion of MgPdAl-LDH-Gly (dispersed in one of the three solvents mentioned above at concentration of 1 mg/mL) were added in a 25 mL flask with a reflux condenser, followed by four times degassing under a vacuum pump and flushing with nitrogen. The mixture was stirred and heated at 130 °C for 4 h, and then cooled to room temperature, extracted with ethyl ether (3  $\times$  10 mL), and washed with brine (3  $\times$  25 mL). The combined organic layer was separated, dried over MgSO $_4$ , and then the conversion was determined by gas chromatography (HP-1102) equipped with a 30 m capillary column (CEC-1). The injector and FID detector were set at 250 and 260 °C, respectively. The temperature program was set at an initial temperature of 100 °C, and a final temperature of 240 °C with a heating rate of 20 °C/min.

## 2.4. Recycling of the delaminated MgPdAl-LDH catalyst

In the recycling test, 0.5 g 400 mesh silica were used to capture the *in situ* formed Pd(0) species in the initial run of reaction between bromobenzene and styrene. After completion of the first run, lightly grey silica was obtained by filtering and washing with acetone and applied to the next run.

## 2.5. General procedure for the Heck reaction

After the initial optimization studies with bromobenzene and styrene, we conducted the reaction a wide variety of aryl halides with styrene in the presence of the new catalyst system. Typically, 1 mL FA-delaminated MgPdAl-LDH-Gly (the concentration of

MgPdAl-LDH-Gly depends on the reactions needed, 1 mg MgPdAl-LDH-Gly contains  $2.5 \times 10^{-7}$  mol Pd) was diluted by 6 mL DMF and 0.5 mL H $_2$ O. Then 5 mmol aryl halides, 6 mmol styrene (for multi-halides, styrene should be doubled or trebled) and 6 mmol NaOAc were added. The mixture was stirred at 130 °C for 4–20 h, then cooled to room temperature, extracted with ethyl ether (3  $\times$  10 mL), and washed with brine (3  $\times$  25 mL). The combined organic layer was separated, dried over MgSO $_4$ , and evaporated to give the product. The residue, if necessary, was purified by column chromatography or recrystallized to give the corresponding products. All of the products were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectroscopy.

## 3. Results and discussion

### 3.1. Optimization of synthesis parameters and delamination of nanocrystal MgPdAl-LDH-Gly into nanosheets

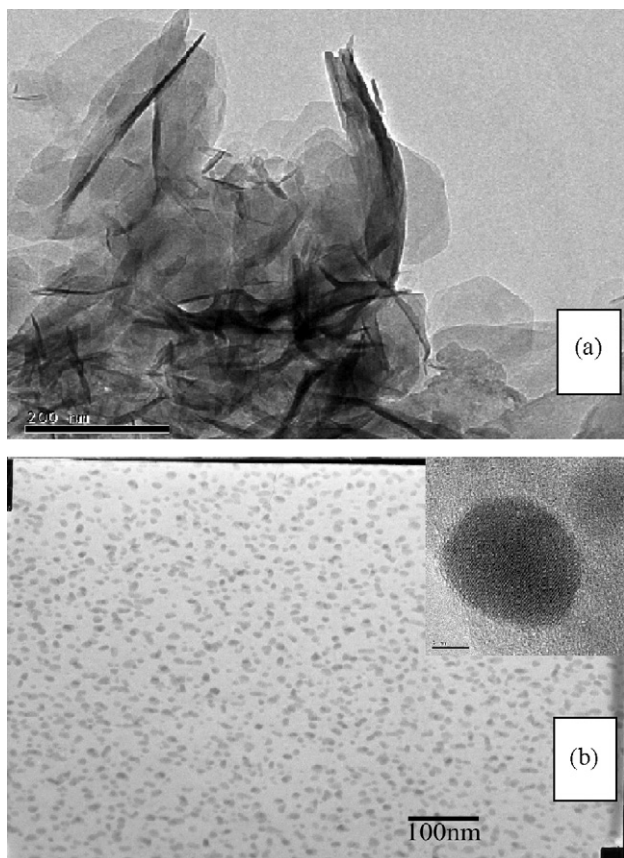
The starting glycinate-intercalated MgPdAl-LDH with (Mg + Pd)/Al = 3.0 (MgPdAl-LDH-Gly) was prepared by co-precipitation. Although palladium(II) has a tendency to show square planar rather than octahedral coordination, it has been previously suggested that small amounts of octahedral palladium(II) with an atomic ratio no more than 5% can still be incorporated into the LDH layers by co-precipitation method [42,49]. To avoid formation of other phases, we chose 0.95/0.05/0.33 as Mg $^{2+}$ /Pd $^{2+}$ /Al $^{3+}$  atomic ratio for the starting solution. Delamination testings of MgPdAl-LDH-Gly were carried out in *N,N*-dimethylformamide (DMF) and formamide (FA) [18], respectively. Treatment of MgPdAl-LDH-Gly with FA at room temperature yielded a light brown transparent colloidal solution, and no sediment was observed upon standing, indicating that total delamination of MgPdAl-LDH-Gly took place in FA; and once delaminated, the single lamellas of LDH were solvated and thus stabilized by FA. In contrast, even the ultrasonic treatment with the DMF dispersion of MgPdAl-LDH-Gly just resulted in a turbid solution, suggesting that MgPdAl-LDH-Gly could not be delaminated completely in single solvent of DMF. Interestingly, further addition of formamide into this turbid dispersion just followed by hand shaking, the turbid dispersion turned into a transparent colloidal solution immediately (Fig. 1). Owing to the colloidal nature of the LDH mono-lamellas, dispersion (b) might act as a much better catalyst in Heck reaction than dispersion (a). The easy delamination of MgPdAl-LDH-Gly pre-dispersed by DMF also suggested the pre-swell took place in DMF before adding FA into. This swelling effect might result from the incorporation of the solvents into the interlayers [16,25]. For the purpose of catalysis, the swollen LDH layers with enough enlarged basal spacing may provide reactants with free access to the inner surface of brucite-like sheets.

### 3.2. Characterizations

The XRD pattern of the as-prepared MgPdAl-LDH-Gly shows that the sample was mainly a hydrotalcite-like structure (see Supporting Information, Fig. S1a). The basal spacing for glycinate-intercalated MgPdAl-LDH, around 0.8 nm, is consistent with the reported data [56]. Compared with the starting MgPdAl-LDH-Gly, the XRD pattern of the glue-like solid obtained from the centrifugal treatment of FA dispersion shows the absence of sharp basal peaks (Fig. S1b). This indicates that the host sheets were no longer in parallel with each other in constant distance, implying delamination of the MgPdAl-LDH [18].

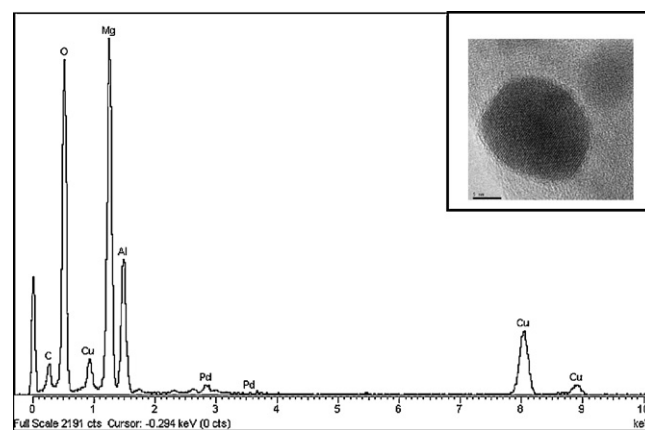
A typical TEM image of MgPdAl-LDH-Gly dispersed in ethanol shows that the LDH nanocrystals were heavily aggregated (Fig. 2a); single crystals of LDH were not observed in this original struc-





**Fig. 2.** TEM images of the MgPdAl-LDH-Gly from (a) the ethanol dispersion and (b) the FA dispersion (inset: HRTEM image of a single nanosheet, the scale bar is 5 nm).

ture of LDH [9]. However, the TEM image of the MgPdAl-LDH-Gly dispersed in FA shows mono-dispersed thin sheets sized in  $\sim 11$  nm (Fig. 2b). Compared with the stacking ones (Fig. 2a), these nanosheets look more faint and uniform in contrast, which is compatible with the ultrathin thickness of the delaminated layers (0.7–1.3 nm) [21]. Both lateral size and thickness of these delamination-derived MgPdAl-LDH monolayers are in nanometer range, which would greatly favor the catalytic application. The TEM image also shows these nanosheets of LDH are not uniform in shape, implying occurrence of some fracture of the LDH sheets during the delamination. The HRTEM image of individual nanosheets (inset of Fig. 2b) reveals ordered lattice fringes with fringe separation of



**Fig. 3.** EDX analysis of individual MgPdAl brucite-like ultrathin sheet. The peaks of Cu and C come from the copper grid and carbon film substrate, respectively (inset: HRTEM image of a single nanosheet, the scale bar is 5 nm).

about 0.310 nm. This larger cell parameter compared with the in-plane structural parameter of MgAl-LDH crystals ( $a = 0.306$  nm) can be attributed to the presence of the larger  $\text{Pd}^{2+}$  in brucite-like layers [42]. Furthermore, EDX analysis of these ultrathin sheets (Fig. 3) also reveals homogeneous distribution of the constitute metals on individual layers and the calculated Pd(II)/Mg(II)/Al ratios was 5/92/34, which agrees well with that (5/95/33) of the starting solutions. This result indicates Pd was exactly incorporated into the single lamellas of LDH. In addition, the TEM image of the FA-dispersed MgAl-LDH-Gly shows no obvious difference with that of FA-dispersed MgPdAl-LDH-Gly (see Supporting Information, Fig. S2), implying that the implantation of Pd has no impact on the delamination.

### 3.3. Catalytic performance of the delaminated MgPdAl-LDH

In the present work, the catalytic activity of MgPdAl-LDH-Gly was examined in the Heck coupling reaction. The coupling of bromobenzene with styrene was chosen as a model reaction. Initially, the catalytic performances of MgPdAl-LDH-Gly toward this reaction were examined in solvents of DMF and FA, respectively, which were performed at the same conditions and the same level of palladium loading. DMF and FA dispersions of MgPdAl-LDH-Gly showed the low and moderate activities for the reaction between bromobenzene and styrene, respectively (Table 1, Entries 1 and 2). DMF is a commonly used solvent for organic reactions (including Heck reactions) due to its high boiling point and good solubility for a large scope of organic substances, but the MgPdAl-LDH-Gly

**Table 1**

Optimization of reaction conditions using the coupling of bromobenzene and styrene as model reaction<sup>a</sup>

Entry	Catalyst	mol% Pd	Yields (%)	TOF
1	10 mL DMF-dispersed MgPdAl-LDH-Gly <sup>b</sup>	0.025	42	420
2	10 mL FA-delaminated MgPdAl-LDH-Gly <sup>b</sup>	0.025	62	620
3	8 mL DMF-dispersed MgPdAl-LDH-Gly + 2 mL FA <sup>c</sup>	0.025	100	1,000
4	1 mL FA-delaminated MgPdAl-LDH-Gly + 6 mL DMF <sup>d</sup>	0.0025	100	10,000
5	1 mL FA-delaminated MgPdAl-LDH-Gly + 6 mL NMP <sup>d</sup>	0.0025	100	10,000
6	Pd(II) supported on MgAl-LDH <sup>e</sup>	0.5	40	20
7	Delaminated MgAl-LDH-Gly <sup>f</sup>	0	0	0

<sup>a</sup> All reactions were performed at 130 °C for 4 h, 10 mmol of bromobenzene, 12 mmol of styrene, 0.5 mL H<sub>2</sub>O and 1.6 g of NaOAc were used for all reactions.

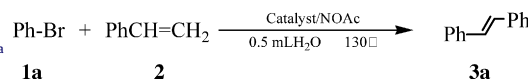
<sup>b</sup> Dispersions of MgPdAl-LDH-Gly at concentration of 1 mg/mL.

<sup>c</sup> 8 mL DMF dispersion of 10 mg MgPdAl-LDH-Gly followed by addition of 2 mL pure FA.

<sup>d</sup> 1 mL FA-delaminated MgPdAl-LDH-Gly (1 mg/mL) diluted by 6 mL pure DMF or NMP.

<sup>e</sup> Catalysts dispersed in mixture of 1 mL FA, 6 mL DMF and 0.5 mL water.

<sup>f</sup> 2 mL FA-delaminated MgAl-LDH-Gly diluted by 8 mL pure DMF.



crystals dispersed in DMF will exist as aggregated form as a result of the limited delaminating ability of DMF, which led to the limited accessibility to the inner surface of the MgPdAl-LDH. Although the MgPdAl-LDH-Gly could be delaminated into mono-lamellas by FA (Fig. 2b), the catalytic activity of FA-dispersed MgPdAl-LDH-Gly is not as high as we expected (Entry 2). The limited solubility of FA led to a binary-phase between reactants and FA which was used solely as medium of delamination and reaction. Therefore, DMF and FA are complementary each other in the solubility and the capability of delamination; combination of using both solvents is necessary to improve the catalytic performance of the MgPdAl-LDH nanosheets.

As expected, the catalytic performance of DMF-dispersed MgPdAl-LDH-Gly exhibited much better activity when small amount of FA was added (Table 1, Entry 3), indicating that the access of reactant molecules to Pd sites was largely increased with the delaminating effect of FA on MgPdAl-LDH-Gly. Because the catalytic activity was improved with the increase of the accessible inner surface of LDH, the catalysis might be a heterogeneous process occurring on the surface of colloidal LDH mono-lamellas [35,43]. In the other word, the enhanced catalytic activity was well correlated with the delamination of MgPdAl-LDH layers.

Inspired by such an interesting observation, we lowered the Pd loading further. One millilitre of FA-delaminated MgPdAl-LDH was diluted by 6 mL DMF. With improved solubility for the reactant molecules, it was found that these colloidal ultrathin sheets of MgPdAl-LDH (Fig. 1b) exhibited excellent catalytic activity toward Heck reaction. The optimal amount of Pd could be reduced as low as 0.0025%; the turnover number (TON, moles of substrate converted/moles of Pd) and turnover frequency (TOF, TON per hour) for the reaction between bromobenzene and styrene are about 40,000 and  $10,000\text{ h}^{-1}$ , respectively (Table 1, Entry 4). Earlier reports suggest that metal colloids could be stabilized by some solvents such as acetone [57], DMF [58], propylene carbonate [59] and *N*-methylpyrrolidinone (NMP) [60]. In the present study, FA-delaminated MgPdAl-LDH diluted by NMP was also tested for catalysis, and the same activity as that of DMF was also obtained (Entry 5, Table 1).

Pd(II) supported on MgAl-LDH [39] was also evaluated for its catalytic activities for comparison with the delaminated MgPdAl-LDH. As shown in Table 1 (Entry 6), the catalytic activity of this catalyst for the same Heck reaction were much lower than that of the delaminated MgPdAl-LDH. The TONs for Pd(II)/MgAl-LDH were 80, in contrast with TON of 40,000 for the delaminated MgPdAl-LDH. Conventional MgAl-LDH nanosheets without Pd implantation did not yet show catalytic activity toward Heck reaction (Entry 7, Table 1).

The outstanding catalytic performance of delaminated MgPdAl-LDH for Heck reaction can be attributed to the following factors. Compared with the single Pd(II) salts, these colloidal LDH mono-layers were bifunctional, i.e., they contained basic sites as well as catalytically active palladium sites. On the other hand, differing from the conventionally supported Pd (Table 1, Entry 6), these two kinds of sites on the brucite-like nanosheets were combined at an atomic level because of the co-precipitation method employed and present a synergic effect; so the basic sites on the MgPdAl-LDH mono-lamellas might act as basic ligands. It was reported that the basic supports for Pd or Pt favors activation of Ar–X bonds [43,61–65]. The electron-rich environment derived from basic sites of LDH layers would provide the requisite electron density on palladium to undergo oxidative addition of the *in situ* formed Pd(0) with haloarene [66], which plays a key role in activation of C–X bonds. It is worth noting that the Pd(II) was reduced to Pd(0) *in situ* under the reaction condition employed [67]. These *in situ* formed Pd(0) species implanted in the brucite-like layers were homogeneously separated from each other by the Mg, Al and OH<sup>−</sup> on

the lamellas, hence the further growth of the formed Pd(0) nuclei was effectively hindered and terminated at an early stage [68], accounting for the highly catalytic efficiency [69]. Furthermore, the pre-implantation of Pd(II) into LDH also helps to prevent the *in situ* formed Pd(0) from extraction from the mono-lamellas followed by Pd-black formation [70,71]. Although the mechanism of heterogeneously catalyzed Heck reactions still remains in debate [72,73], it is commonly accepted that the Pd-black formation will lead to the suppression of the catalytic process.

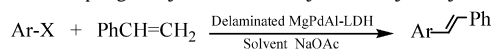
#### 3.4. Tests of reusability for the delaminated MgPdAl-LDH

In our case, it is hard to recycle the catalyst by simple filtering or centrifugation because of the ultrathin and ultra-small nature of the delaminated LDH, and the ultra-low catalyst loading. Therefore, 400 mesh silica was used to capture the *in situ* formed Pd(0) species during the initial catalytic reaction. Similar procedure for immobilization of Pd(0) on silica was also previously reported [74]. After completion of the first run, lightly grey silica were obtained by filtering, then washed it and applied to the next run. As compared to the initial run, this silica-captured Pd(0) showed a 90% loss in catalytic activity (evaluated by TON and TOF), indicating that freshly formed Pd(0) clusters might be the actual sites of catalysis. Reetz and Lohmer also reported the similar loss of activity when Al<sub>2</sub>O<sub>3</sub> was applied to capture the PC-stabilized Pd(0) clusters [59]. The freshly formed Pd(0) clusters have more defect sites, steps and kinks compared with the recycled ones [75–78]. Of course, the decreased activity may also be due to the partial breakage of the brucite-like structure at the end of the initial run, which led to the inevitable separation of the Pd sites from basic sites. Even so, the delaminated MgPdAl-LDH can still be defined as a highly effective catalyst; a conventional heterogeneous catalyst even with a 0.25% Pd loading would have to be re-used 100 times to achieve the same TON as the delaminated MgPdAl-LDH with a 0.0025% Pd loading (Table 1, Entry 4).

#### 3.5. Reactivity of various aryl halides

After the initial optimization studies with bromobenzene and styrene, we conducted the reactions of a wide variety of aryl halides with styrene (Table 2) under this new catalytic system. In all cases *E* isomers were obtained exclusively. The conversion in the reactions depended on the nature of the halides and their substituents. The best result was obtained in the reaction with the highly reactive iodobenzene (Entry 13 of Table 2: ca. 100,000 TON in 4 h). A large variety of aryl bromides with deactivated groups such as OH and OCH<sub>3</sub> were also reactive in this catalytic system. Interestingly, the sterically hindered 1,2-dibromobenzene could be di-coupled with styrene in 88% yield. Moreover, in the coupling of 1,4-dibromobenzene with styrene at the molar ratio of 1 (1,4-dibromobenzene to styrene), the expected 1-bromo-4-styrylbenzene was not obtained; but the di-coupled product (1,4-di-styrylbenzene) was exclusively obtained instead. Similar phenomena were also observed in the cases of 1,3,5-tribromobenzene and 1-bromo-4-iodobenzene, indicating that the *in situ* formed intermediate 1-bromo-4-styrylbenzene was even more reactive than 1-bromo-4-iodobenzene and the equilibrium shifts to the formation of a more conjugated molecule. The multi-coupling of multi-bromobenzene by styrene might be thermodynamically driven by forming higher conjugated molecules which have lower total energy compared with their lowly conjugated counterparts.

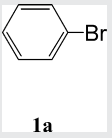
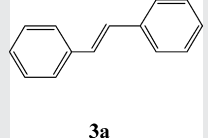
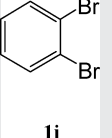
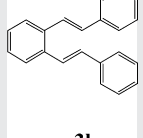
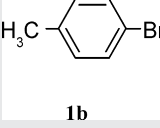
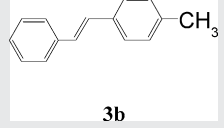
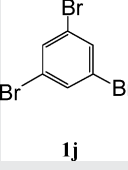
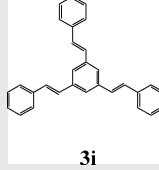
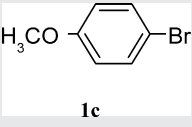
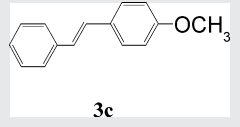
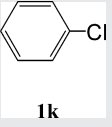
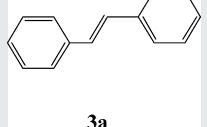
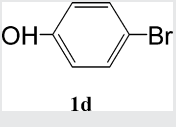
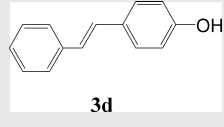
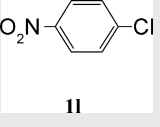
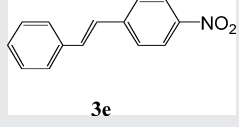
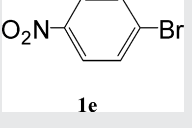
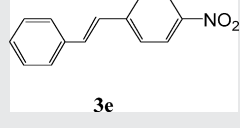
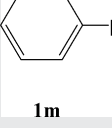
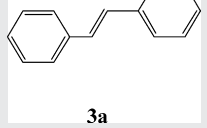
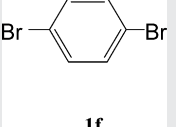
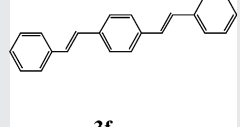
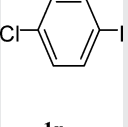
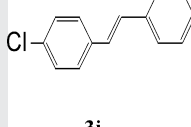
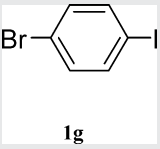
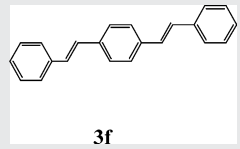
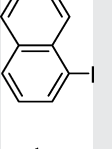
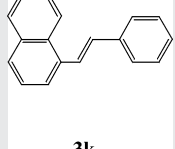
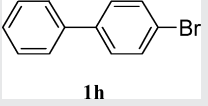
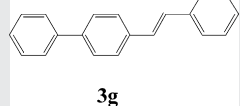
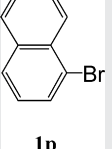
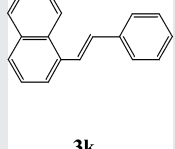
As for the chlorobenzene, the coupling reaction afforded only 25% yield even at a higher loading of Pd and a longer reaction time (20 h); some diphenyl was also found in the products because of the

**Table 2**Heck coupling of aryl halides with styrene catalyzed by delaminated MgPdAl-LDH-Gly under optimized conditions<sup>a</sup>

1a ~ 1p

2

3a ~ 3k

Entry	ArX	Product	mol% Pd	Yield% <sup>b</sup>	Entry	ArX	Product	mol% Pd	Yield% <sup>b</sup>
1			0.0025	100 <sup>c</sup>	9			0.005	88
2			0.0025	95	10			0.0075	95
3			0.0025	98	11			0.05	25 <sup>c,d,e</sup>
4			0.005	90	12			0.05	70 <sup>d,e</sup>
5			0.0025	96	13			0.001	100 <sup>c</sup>
6			0.005	94	14			0.001	98
7			0.005	96	15			0.0025	96
8			0.0025	95	16			0.005	80

<sup>a</sup> Reaction conditions: 5 mmol aryl halide, 6 mmol styrene, 6 mmol NaOAc, 1 mL FA-delaminated MgPdAl-LDH-Gly diluted by 6 mL DMF and 0.5 mL H<sub>2</sub>O, 130 °C, 4 h.<sup>b</sup> Yield of isolated product.<sup>c</sup> Yields of product from GC analysis.<sup>d</sup> 1 mL FA-delaminated MgPdAl-LDH-Gly diluted by 6 mL NMP.<sup>e</sup> Reaction time: 20 h.

homo-coupling between chlorobenzene. As expected, better results were obtained in the presence of activated aryl halides such as 4-bromonitrobenzene and 4-chloronitrobenzene (Table 2, Entries 5 and 12).

#### 4. Conclusion

In summary, we provide herein a new alternative pre-catalyst of palladium for Heck reaction. The semi-heterogeneous delaminated colloidal  $\text{Mg}_{0.95}\text{Pd}_{0.05}\text{Al}_{1/3}$ -LDH catalyst (ligand-free), which catalyzed efficiently the coupling reaction of a variety of aryl halides with styrene, was characterized by XRD, TEM, HRTEM and EDX analysis. These bifunctional LDH mono-lamellas contain basic sites and catalytically active palladium sites which interact with each other closely. And the benefit of site accessibility by delamination has been shown catalytically. We demonstrated experimentally, for the first time, that the catalytic activities and the extents of the delamination of LDH are well correlated. This first attempt will open up catalytic applications of the delaminated LDHs. More systematic investigation on the catalytic aspects of the delaminated LDHs bearing the transition metals other than Pd(II) will be further reported by us.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.05.003.

#### References

- [1] M.L. Kantam, S. Roy, M. Roy, B. Sreedhar, B.M. Choudary, R. Lal De, J. Mol. Catal. A: Chem. 273 (2007) 26.
- [2] S.K. Jana, P. Wu, T. Tatsumi, J. Catal. 240 (2006) 268.
- [3] K.M. Parida, N. Baliarsingh, B. Sairam Patra, J. Das, J. Mol. Catal. A: Chem. 267 (2007) 202.
- [4] F. Leroux, J.-P. Besse, Chem. Mater. 13 (2001) 3507.
- [5] S.-Y. Kwak, W.M. Kriven, M.A. Wallig, J.-H. Choy, Biomaterials 25 (2004) 5995.
- [6] L. Albiston, K.R. Franklin, E. Lee, J.B.A.F. Smeulder, J. Mater. Chem. 6 (1996) 871.
- [7] Y. Zhao, F. Li, R. Zhang, D.G. Evans, X. Duan, Chem. Mater. 14 (2002) 4286.
- [8] Z.P. Xu, G.S. Stevenson, C.-Q. Lu, G.Q. Lu, P.F. Bartlett, P.P. Gray, J. Am. Chem. Soc. 128 (2006) 36.
- [9] Z.P. Xu, G. Stevenson, C.-Q. Lu, G.Q. Lu, J. Phys. Chem. B 110 (2006) 16923.
- [10] S. Liu, J. Zhang, N. Wang, W. Liu, C. Zhang, D. Sun, Chem. Mater. 15 (2003) 3240.
- [11] E. Gardner, K.M. Huntoon, T.J. Pinnavaia, Adv. Mater. 13 (2001) 1263.
- [12] D.G. Evans, X. Duan, Chem. Commun. (2006) 485.
- [13] L. Wang, C. Li, M. Liu, D.G. Evans, X. Duan, Chem. Commun. (2007) 123.
- [14] M. Adachi-Pagano, C. Forano, J.-P. Besse, Chem. Commun. (2000) 91.
- [15] F. Leroux, M. Adachi-Pagano, M. Intissar, S. ChauvieÁre, C. Forano, J.-P. Besse, J. Mater. Chem. 11 (2001) 105.
- [16] M. JobbÁgy, A.E. Regazzoni, J. Colloid Interf. Sci. 275 (2004) 345.
- [17] S. O'Leary, D. O'Hare, G. Seeley, Chem. Commun. (2002) 1506.
- [18] T. Hibino, W. Jones, J. Mater. Chem. 11 (2001) 1321.
- [19] T. Hibino, M. Kobayashi, J. Mater. Chem. 15 (2005) 653.
- [20] Q. Wu, A. Olafsen, Ø.B. Vistad, J. Roots, P. Norby, J. Mater. Chem. 15 (2005) 4695.
- [21] L. Li, R. Ma, Y. Ebina, N. Iyi, T. Sasaki, Chem. Mater. 17 (2005) 4386.
- [22] C. Jaubertie, M.J. Holgado, M.S. San Roman, V. Rives, Chem. Mater. 18 (2006) 3114.
- [23] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, J. Am. Chem. Soc. 128 (2006) 4872.
- [24] R. Ma, Z. Liu, K. Takada, N. Iyi, Y. Bando, T. Sasaki, J. Am. Chem. Soc. 129 (2007) 5257.
- [25] K. Okamoto, T. Sasaki, T. Fujita, N. Iyi, J. Mater. Chem. 16 (2006) 1608.
- [26] Z. Liu, R. Ma, Y. Ebina, N. Iyi, K. Takada, T. Sasaki, Langmuir 23 (2007) 861.
- [27] A. Corma, U. Diaz, M.E. Domine, V. Fornés, J. Am. Chem. Soc. 122 (2000) 2804.
- [28] A. Corma, V. Fornés, J.L. Jordá, F. Rey, R. Fernandez-Lafuente, J.M. Guisan, C. Mateo, Chem. Commun. (2001) 419.
- [29] B. Pawelec, S. Murcia-Mascaros, J.L.G. Fierro, Langmuir 18 (2002) 7953.
- [30] A. Corma, V. Fornés, U. Diaz, Chem. Commun. (2001) 2642.
- [31] P. Wu, D. Nuntasri, J. Ruan, Y. Liu, M. He, W. Fan, O. Terasaki, T. Tatsumi, J. Phys. Chem. B 108 (2004) 19126.
- [32] B.M. Choudary, V.S. Jaya, B.R. Reddy, M.L. Kantam, M.M. Rao, S.S. Madhavendra, Chem. Mater. 17 (2005) 2740.
- [33] A. Dubey, Green Chem. 9 (2007) 424.
- [34] R.F. Heck, Palladium Reagents in Organic Syntheses, Academic Press, London, 1985.
- [35] F. Prinetto, M. Manzoli, G. Ghiotti, M.J.M. Ortiz, D. Tichit, B. Coq, J. Catal. 222 (2004) 238.
- [36] S.K. Jana, Y. Kubota, T. Tatsumi, Stud. Surf. Sci. Catal. 165 (2007) 701.
- [37] J.R. Ruiz, C.J. Sanchidrian, M. Mora, Tetrahedron 62 (2006) 2922.
- [38] J.R. Ruiz, C.J. Sanchidrian, M. Mora, J. Fluor. Chem. 127 (2006) 443.
- [39] H. Zhou, G.L. Zhuo, X. Jiang, J. Mol. Catal. A 248 (2006) 26.
- [40] N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, J. Org. Chem. 66 (2001) 6620.
- [41] B.M. Choudary, M.L. Kantam, N.M. Reddy, N.M. Gupta, Catal. Lett. 82 (2002) 79.
- [42] T. Nishimura, N. Kakiuchi, M. Inoue, S. Uemura, Chem. Commun. (2000) 1245.
- [43] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14128.
- [44] F. Basile, G. Fornasari, M. Gazzano, A. Vaccari, Appl. Clay Sci. 16 (2000) 185.
- [45] T.H. Bennur, A. Raman, R. Bal, B.M. Chanda, S. Sivasanker, Catal. Commun. 3 (2002) 493.
- [46] S. Narayanan, K. Krishna, Catal. Today 49 (1999) 57.
- [47] M. Komiyama, Catal. Rev. Sci. Eng. 27 (1985) 341.
- [48] J.W. Geus, J.A.R. van Veen, Preparation of Supported Catalysts, Elsevier, Amsterdam, 1993.
- [49] F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifiro, A. Vaccari, J. Chem. Soc. Chem. Commun. (1996) 2435.
- [50] B.C. Zhu, X. Jiang, Appl. Organomet. Chem. 21 (2007) 345.
- [51] R.F. Heck, J.P. Nolley Jr., J. Org. Chem. 37 (1972) 2320.
- [52] J.E. Plevyak, R.F. Heck, J. Org. Chem. 43 (1978) 2454.
- [53] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
- [54] Y. Mori, M. Seki, J. Org. Chem. 68 (2003) 1571.
- [55] S.S. Pröckl, W. Kleist, M.A. Gruber, K. Köhler, Angew. Chem. Int. Ed. 43 (2004) 1881.
- [56] T. Hibino, Chem. Mater. 16 (2004) 5482.
- [57] G.C. Trivino, K.J. Klabunde, E.B. Dale, Langmuir 3 (1987) 986.
- [58] S.-T. Lin, M.T. Franklin, K.J. Klabunde, Langmuir 2 (1986) 259.
- [59] M.T. Reetz, G. Lohmer, Chem. Commun. (1996) 1921.
- [60] M.T. Reetz, E. Westermann, Angew. Chem. Int. Ed. 39 (2000) 165.
- [61] M.L. Kantam, S. Roy, M. Roy, B. Sreedhar, B.M. Choudary, Adv. Synth. Catal. 347 (2005) 2002.
- [62] A. Cwik, Z. Hell, F. Figueras, Adv. Synth. Catal. 348 (2006) 523.
- [63] M.L. Kantam, K.B.S. Kumar, P. Srinivas, B. Sreedhar, Adv. Synth. Catal. 349 (2007) 1141.
- [64] A. Cwik, Z. Hell, F. Figueras, Org. Biomol. Chem. 24 (2005) 4307.
- [65] B.M. Choudary, M. Roy, S. Roy, M.L. Kantam, J. Mol. Catal. A: Chem. 241 (2005) 215.
- [66] G. Zou, W. Huang, Y. Xiao, J. Tang, New J. Chem. 30 (2006) 803.
- [67] Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang, M. Zhou, J. Org. Chem. 71 (2006) 4339.
- [68] Similar effect was also reported previously. See: Y. Guo, H. Zhang, Y. Wang, Z.-L. Liao, G.-D. Li, J.-S. Chen, J. Phys. Chem. B 109 (2005) 21602.
- [69] M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559.
- [70] L. Djakovitch, K. Koehler, J. Am. Chem. Soc. 123 (2001) 5990.
- [71] M.D. Smith, A.F. Stepan, C. Ramarao, P.E. Brennan, S.V. Ley, Chem. Commun. (2003) 2652.
- [72] L.X. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133.
- [73] N.T.S. Phan, M.V.D. Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609.
- [74] M. Ganesan, R.G. Freemantle, S.O. Obare, Chem. Mater. 19 (2007) 3464.
- [75] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732.
- [76] R. Narayanan, M.A. El-Sayed, Nano Lett. 4 (2004) 1333.
- [77] J. Le Bars, U. Specht, J.S. Bradley, D.G. Blackmond, Langmuir 15 (1999) 7621.
- [78] R. Narayanan, M.A. El-Sayed, Langmuir 21 (2005) 2027.