

# Heck reaction catalyzed by Pd supported on LDH-F hydrotalcite

Hao Zhou<sup>a</sup>, Guang Lan Zhuo<sup>b</sup>, Xuan Zhen Jiang<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, PR China

<sup>b</sup> Department of Applied Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310027, PR China

Received 29 September 2005; received in revised form 8 December 2005; accepted 12 December 2005

Available online 18 January 2006

## Abstract

LDH-F hydrotalcite was used, for the first time, as an efficient and selective basic support for palladium catalyzed Heck reaction. The ligand-free heterogeneous catalyst Pd/LDH-F exhibits higher activity and selectivity in the Heck reaction of aryl bromides with styrene on small amount of palladium (0.1 mol% of Pd). The higher yields than those previously obtained with Pd containing layered double hydroxides (LDHs) are reached. The catalyst can easily be separated from the reaction mixture and reused after washing without loss in activity. The influence of the highly polarized basic fluoride ions on reaction performance is discussed in this study. Moreover, the influence of several fundamental parameters (nature of support, Mg/Al ratio, property of the Pd complex) on the reactivity is also discussed.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Heck reaction; Aryl halides; LDH-F supported palladium catalyst; Hydrotalcite

## 1. Introduction

The Heck reaction, a palladium-catalyzed carbon–carbon bond formation between aryl halides and olefins, became an excellent tool for the synthesis of elaborated styrene derivatives due to its wide variety of functional groups on both reactants and the broad availability of aryl bromides and chlorides [1–3] (Scheme 1). In the past few years, palladium complexes mostly catalyzed the Heck reaction with phosphine ligands in homogeneous system [4–7]. The heterogeneous Pd catalyst systems are also active in the Heck reaction; however, they are not always as reactive as homogeneous catalysts. Regarding industrial applications, however, the homogeneous catalysts are expensive (Pd, phosphines or special ligand systems) and only very few experiments were reported about their separation from the reaction mixture and reuse. It is highly desirable to develop a ligandless, recyclable new heterogeneous catalyst system to dispense with the use of expensive and air-sensitive basic phosphines for the Heck reactions of aryl halides catalyzed by palladium catalysts.

In efforts to develop a heterogeneous catalyst system for the Heck reaction, and its complexes supported on a variety of solids,

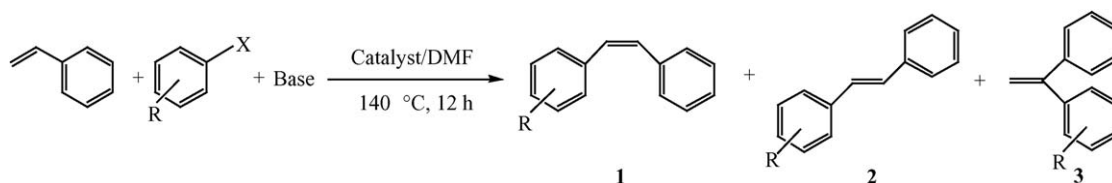
particularly, active carbon [8,9], mesoporous silica [10], inorganic oxide [11,12], molecular sieves [13,14], polymers [15,16], zeolites [17], hydrotalcites [18,21] and even capsule [19], etc., have been intensively studied. In these studies, lots of acid supports (e.g. molecular sieves and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) have been utilized on supported palladium catalysts in Heck reaction. However, it was found that the basic supports performed higher catalytic activity than that on the acidic supports. For example, Pd/MgO [20] in the Heck reaction resulted in high conversion albeit poor selectivity. Choudary et al. [21] have applied the layered double hydroxide supported nanopalladium catalysts in the coupling reaction. Their results indicated that the basic support, LDHs, facilitated the oxidative addition of Pd<sup>0</sup> with aryl halides and eventually the Heck reaction. The strong basic KF-Al<sub>2</sub>O<sub>3</sub> [22] has been already applied in the cross-coupling reactions as the support for supported palladium catalyst with fairly high yield.

The choice of layered double hydroxide fluoride (LDH-F) as the basic support was motivated by the following reasons: not only to stabilize the palladium particles but also to provide the adequate electron density to the anchored Pd<sup>0</sup> species to facilitate the oxidative addition of the aryl halides.

In the present study, higher yields and selectivity than those previously obtained with Pd containing layered double hydroxides (LDHs) were reached for the Heck reaction catalyzed by palladium supported on LDH-F (Pd/LDH-F). The strong basic solid KF- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the analogues modified by potassium

\* Corresponding author.

E-mail address: [chejiang@zju.edu.cn](mailto:chejiang@zju.edu.cn) (X.Z. Jiang).



Scheme 1.

fluoride were also applied as the supports for the supported palladium catalysts and exhibited better activity than that on the raw supports.

## 2. Experimental

### 2.1. Reagents

Bromobenzene, styrene and DMF (Shanghai Chemical Reagent Company) were dried with 4A molecular sieves. Silica,  $\gamma$ - $\text{Al}_2\text{O}_3$ , NaY and  $\text{NH}_4\text{Y}$  were purchased from Shanghai Chemical Reagent Company and used as received. The hydrotaalcites (LDH- $\text{CO}_3$  and LDH-F) were prepared according to the literature [23].

### 2.2. Catalyst preparation

#### 2.2.1. Preparation of $\text{Pd}^{\text{II}}$ /support and Pd/support

4.7 ml solution of  $\text{H}_2\text{PdCl}_4$  (0.01199 g/mL) was slowly added dropwise to the 1 g dry support (such as LDH-F) with a microneedle to achieve high Pd dispersion as possible. The  $\text{Pd}^{\text{II}}$ /support was obtained after dried. Then the dried solid was reduced with hydrazine hydrate (1 g, 20 mmol) in absolute ethyl alcohol (20 mL) for 12 h at room temperature, filtered, washed with absolute ethyl alcohol, and vacuum-dried to give Pd/support (5%, w/w) catalyst.

#### 2.2.2. Preparation of $\text{Pd}(\text{OAc})_2$ /support and PdPc/support

A solution of the palladium compound (such as  $\text{Pd}(\text{OAc})_2$ ) in THF was added dropwise to a suspension of the support in THF (20 mL of support). The mixture was stirred for 3 days at room temperature. The THF in the solution was removed in a rotary evaporator. The remainder was further vacuum-dried to give the catalyst of Pd compound loading on the support.

#### 2.2.3. Preparation of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ /support

A 0.1 M ammonia solution of  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$  prepared from  $\text{PdCl}_2$  and a commercial ammonia solution was added dropwise to a suspension of the support in bi-distilled water (100 mL/g of support). The mixture was stirred for 24 h at room temperature, and then it was filtered off and washed until no trace of chloride was detected in the filtration ( $\text{AgNO}_3$  test). The support was vacuum-dried to give a slightly yellow material.

#### 2.2.4. Preparation of the support modified by potassium fluoride

A dried support (e.g. 15 g  $\gamma$ - $\text{Al}_2\text{O}_3$ ) was mixed with KF (10 g) in 100 mL water, after that water was removed at 50–60 °C in a

rotary evaporator. The impregnated support was further dried in a vacuum dried oven for several hours at 75 °C.

### 2.3. Analysis

The reaction was monitored by gas chromatography (HP-1102) equipped with a 30 m capillary column (CEC-1). The injector and FID detector were set at 250 °C and 260 °C, respectively. The temperature program set at initial temperature of 100 °C and final temperature of 240 °C with a heating rate of 20 °C/min. The products obtained were purified and identified by GC-MS (HP-5973).

### 2.4. Reaction procedure

In an oven-dried three-necked flask with a reflux condenser, palladium catalyst, base, aryl halide, styrene and DMF were added. Followed by four-times degassing under vacuum and flushing with nitrogen, the mixture was stirred and heated to desired temperature. After completion of the reaction the mixture was cooled to room temperature, and then diluted with dichloromethane, filtered and washed with brine. The organic layer was separated, and then dried over  $\text{MgSO}_4$ , finally analyzed by GC. The products were identified by GC-MS.

### 2.5. Typical example

A typical example is as follows: 20 mmol of bromobenzene, 28 mmol of styrene, 22 mmol of NaOAc, 42 mg Pd/LDH-F (0.1 mol% of Pd) and 20 mL DMF were added in an oven-dried three-necked flask with a reflux condenser. Followed by four-times degassing under a vacuum pump and flushing with nitrogen. The mixture was stirred and heated to 140 °C for 12 h under nitrogen. The mixture was cooled to room temperature, then diluted with dichloromethane (50 mL), filtered and washed with brine (3 mL  $\times$  50 mL). The combined organic layer was separated, dried over  $\text{MgSO}_4$ , and then analyzed by GC.

### 2.6. Measurement of Pd leaching

For the determination of the Pd content in solution, the clear filtrate was collected for precise Pd analysis at the end of the reaction. After careful evaporation of the organic compounds the sample was dissolved by aqua regia, diluted and the solution was filtered and analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (IRIS Intrepid II XSP) for the measurement Pd content in solution with a high accuracy.

### 2.7. X-ray diffraction and fluorine content analysis

The X-ray diffraction (XRD) was performed using a Rigaku D/max-rA rotating anode X-ray diffractometer 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.

According to the literature [24], the samples of LDH-Fs were dissolved by nitric acid, diluted and the solution was analysed with spectrophotometer (H721) for the measurement of fluorine content in the hydrotalcites.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The X-ray diffraction (XRD) patterns of catalysts based on hydrotalcites as supports are shown in Fig. 1 in the range of  $2\theta = 2\text{--}70^\circ$ . Their diffraction peaks can be indexed by the JCPDS X-ray diffraction file of no. 22–700. These patterns all showed three strong and sharp diffraction peaks at  $11^\circ$ ,  $23^\circ$  and  $34^\circ$ , which are attributable to the (003), (006), (009) reflections of hydrotalcites. The remarkable double peaks at  $60^\circ$  correspond to the basal (110) reflections that indicated the presence of layer structure stacking in all the samples. The profiles showed that these samples possess a well-crystallized hydrotalcites structure [25]. Compared to the LDH-F, the diffraction peaks of the Pd-supported hydrotalcites at  $40^\circ$  were all intensified because of the presence of palladium. After reaction, the catalyst Pd/LDH-F still displayed the same diffraction profile and the similar intensity. These indicated that the catalyst Pd/LDH-F retained well-crystallized hydrotalcites structure after reaction.

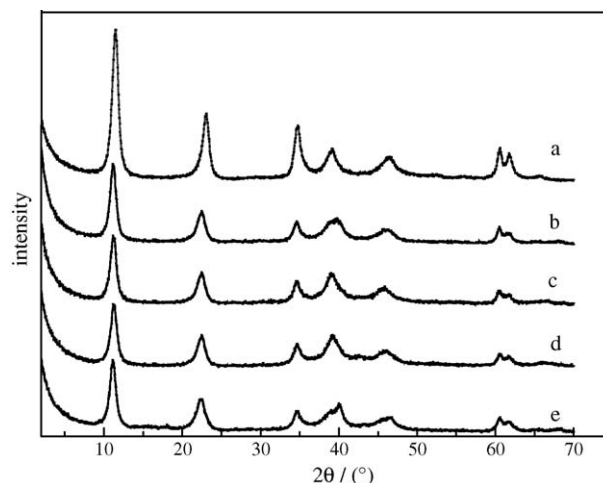


Fig. 1. XRD patterns of different hydrotalcites: (a) LDH-F; (b) Pd/LDH-F; (c) Pd/LDH-F after 1st run; (d) Pd/LDH-F after 2nd run; (e) Pd/LDH-CO<sub>3</sub>, the Mg:Al ratio of hydrotalcites kept at 3:1.

### 3.2. Effect of support

In concerning the effect of support, the experimental results of the Heck reaction catalyzed by various supported palladium catalysts are given in Table 1. For comparing the reactivity of Pd/LDH-F with those of other heterogeneous catalysts, namely Pd/silica, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/NH<sub>4</sub>Y, Pd/NaY and Pd/LDH-CO<sub>3</sub>, in the Heck reaction, separate experiments were conducted under identical conditions with the same ingredients (Entries 1–6). The catalyst Pd/LDH-F exhibits a higher yield (86%) and selectivity (1:2:3 = 0:97:3) than that on the other catalysts in the Heck reaction of bromobenzene with styrene. Though the layered double hydroxide fluoride (LDH-F) has the similar structure as the

Table 1  
The Heck reaction of aryl bromides with styrene catalyzed by various supported palladium catalysts

Entry	R	X	Catalyst	Conv. <sup>a</sup> (%)	All yields <sup>a</sup> (%)
1	H	Br	Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	20	17 (1:2:3 = 1:90:9)
2	H	Br	Pd/silica	42	38 (1:2:3 = 1:92:7)
3	H	Br	Pd/NH <sub>4</sub> Y	40	35 (1:2:3 = 1:91:8)
4	H	Br	Pd/NaY	62	60 (1:2:3 = 1:89:10)
5	H	Br	Pd/LDH-CO <sub>3</sub>	61	58 (1:2:3 = 1:93:6)
6	H	Br	Pd/LDH-F	89	86 (1:2:3 = 0:97:3)
7	H	Br	Pd/KF- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	67	65 (1:2:3 = 1:92:7)
8	H	Br	Pd/KF-silica	65	62 (1:2:3 = 1:91:8)
9	H	Br	Pd/KF-NH <sub>4</sub> Y	68	64 (1:2:3 = 1:90:9)
10	H	Br	Pd/KF-NaY	75	73 (1:2:3 = 1:90:9)
11	4-CH <sub>3</sub>	Br	Pd/LDH-F	57	53 (1:2:3 = 1:93:6)
12	2-CH <sub>3</sub>	Br	Pd/LDH-F	40	35 (1:2:3 = 1:92:7)
13	4-OCH <sub>3</sub>	Br	Pd/LDH-F	60	55 (1:2:3 = 1:93:6)
14	2-Cl	Br	Pd/LDH-F	52	48 (1:2:3 = 1:93:6)
15 <sup>b</sup>	4-NO <sub>2</sub>	Cl	Pd/LDH-F	0	–
16 <sup>b,c</sup>	4-NO <sub>2</sub>	Cl	Pd/LDH-F	17	14 (1:2:3 = 5:88:7)
17 <sup>b,c</sup>	H	Cl	Pd/LDH-F	10	9 (1:2:3 = 4:82:14)

Reaction conditions: aryl halides (1 equiv.), styrene (1.4 equiv.), sodium acetate as base (1.1 equiv.), 0.1 mol% Pd, DMF as solvent, 140 °C, 12 h, nitrogen atmosphere. The Mg:Al ratio of LDH-F and LDH-CO<sub>3</sub> is 3:1.

<sup>a</sup> Conversion of aryl bromides and yields of product from GC analysis.

<sup>b</sup> 0.5 mol% Pd catalyst was used.

<sup>c</sup> PPh<sub>4</sub>Br was used as co-catalyst, the ratio of P/Pd is 10:1.

Table 2

The Heck reaction of aryl bromides with styrene catalyzed by Pd support on LDHs with different ratios of Mg:Al

Entry	Catalyst	Ratio of Mg:Al	Conv. <sup>a</sup> (%)	All yields <sup>a</sup> (%)
1	Pd/LDH-CO <sub>3</sub>	2:1	54	52 (1:2:3 = 1:90:9)
2	Pd/LDH-CO <sub>3</sub>	3:1	61	58 (1:2:3 = 1:93:6)
3	Pd/LDH-CO <sub>3</sub>	4:1	56	55 (1:2:3 = 1:89:11)
4	Pd/LDH-F	2:1	72	69 (1:2:3 = 1:92:7)
5	Pd/LDH-F	3:1	89	86 (1:2:3 = 0:97:3)
6	Pd/LDH-F	4:1	85	83 (1:2:3 = 1:90:9)

Reaction conditions: bromobenzene (1 equiv.), styrene (1.4 equiv.), sodium acetate as base (1.1 equiv.), 0.1 mol% Pd, DMF as solvent, 140 °C, 12 h, nitrogen atmosphere.

<sup>a</sup> Conversion of aryl bromides and yields of product from GC analysis.

LDH-CO<sub>3</sub> hydrotalcite; however, the yield of products was obviously increased from 58% to 86% when by using LDH-F instead of LDH-CO<sub>3</sub> as the support. The strong basic solid KF- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the analogues were also applied as the supports in the Heck reaction catalyzed by these supported palladium catalysts under identical conditions with the same ingredients (Entries 7–10). The results indicate that the nature of support plays a crucial role in reaction performance, such as the supports modified by potassium fluoride exhibit higher activity than that on the untreated supports. The enhancement of support basicity is ascribed to the presence of the loading fluoride ions, which increase the rate of the reaction. The catalyst Pd/LDH-F performs high catalytic activity in Heck reaction in virtue of the polarized basic fluoride ions.

For comparison, we also examined the Heck reaction of other aryl bromides with styrene using the Pd/LDH-F catalyst (Entries 11–14). The catalyst also exhibits fairly high activity and selectivity in the Heck reaction of several aryl bromides with electron-donating group. In the presence of Pd/LDH-F catalyst, a yield of 55% was obtained for the reaction of 4-methoxybromobenzene with styrene (Entry 13). Its activity and selectivity are almost the same level as the catalyst Pd/LDH-CO<sub>3</sub> for the bromobenzene with styrene.

The catalyst Pd/LDH-F was also tested to catalyze the Heck reaction of aryl chlorides. The aryl chlorides are much less reactive than the aryl bromides. In the presence of co-catalyst PPh<sub>4</sub>Br, 9% and 14% yields were obtained for the reaction of chlorobenzene and 4-nitrochlorobenzene with 0.5 mol% Pd, respectively. The reaction of 4-nitrochlorobenzene and styrene even could not occur in the absence of co-catalyst PPh<sub>4</sub>Br.

### 3.3. Influence of the Mg:Al ratio

The hydrotalcites of several different ratios of Mg:Al were investigated in the Heck reaction of aryl bromides with styrene and the results were listed in Table 2. According to literature [25]

the LDHs with different ratios of Mg:Al led to differing basicity. The Pd/LDH-CO<sub>3</sub> catalyst with Mg:Al ratio of 3:1 showed slightly higher activity than that with Mg:Al ratios of 2:1 and 4:1 (Entries 1–3), though the differences were not obvious. In contrast with the catalyst Pd/LDH-CO<sub>3</sub>, the catalysts Pd/LDH-F with Mg:Al ratios of 3:1 and 4:1 (Entries 5 and 6) showed a great disparity compared with Mg:Al ratios of 2:1 (Entry 4), which may be ascribed to the different fluoride contents. Considering the selectivity of the products, the Mg:Al ratio of 3:1 is appropriate for the hydrotalcite as support in the Heck reaction.

The fluorine contents of LDH-Fs with different Mg:Al ratios are given in the Table 3. One can see from Table 3 that the fluorine content increased with raising the ratio of Mg:Al. As the change of ratio of Mg:Al from 2:1 to 4:1, the fluorine content increased from 3.23% to 3.83%. The catalytic activities of these catalysts were affected by the fluorine contents. The results reveal that the highly polarized basic fluoride ions as compensating anions of the LDH support do play an important role in reaction performance of Heck reactions.

### 3.4. Reaction performance of different palladium complexes supported on LDH-F

A comparison of the reactivities of the metallic palladium particles with other palladium ion species supported on LDH-F was presented in Table 4. The results indicate that the catalytic activity of the Pd-modified LDH-F depends on the nature of the complex. The yields (60–70%) were obtained in the Heck reaction catalyzed by [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>/LDH-F and PdPc/LDH-F (Entries 2 and 3). However, the catalysts Pd<sup>I</sup>/LDH-F and Pd/LDH-F performed higher yields (greater than 85%, see Entries 4 and 5). A yield of 89% was achieved by using Pd<sup>I</sup>/LDH-F as the catalyst. In relevant precedent [17], it has been found that the use of polar solvents, particularly DMF, causes the partial leaching of Pd<sup>II</sup> from the solid catalyst to the solution. Owing to the leaching, the catalyst Pd<sup>II</sup>/LDH-F was unable to be recoverable. Therefore,

Table 3

The F<sup>-</sup> content in the LDH-Fs with different ratios of Mg:Al

LDH-F	Ratios of Mg:Al		
	2:1	3:1	4:1
F content (w/w) (%)	3.23	3.62	3.83
All yields (%)	69 (1:2:3 = 1:92:7)	86 (1:2:3 = 0:97:3)	83 (1:2:3 = 1:90:9)

Table 4  
Comparison of reactivity of the Heck reaction of aryl bromides with styrene catalyzed by various catalysts

Entry	Catalyst	Conv. <sup>a</sup> (%)	All yields <sup>a</sup> (%)
1	Pd(OAc) <sub>2</sub> /LDH-F	68	65 (1:2:3 = 1:91:7)
2	[Pd(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> /LDH-F	61	57 (1:2:3 = 1:90:9)
3	PdPc/LDH-F	63	61 (1:2:3 = 1:91:8)
4	Pd <sup>II</sup> /LDH-F	90	89 (1:2:3 = 1:93:6)
5	Pd/LDH-F	89	86 (1:2:3 = 0:97:3)

Reaction conditions: bromobenzene (1 equiv.), styrene (1.4 equiv.), sodium acetate as base (1.1 equiv.), 0.1 mol% Pd, DMF as solvent, 140 °C, 12 h, at nitrogen atmosphere. The Mg:Al ratio of LDH-F kept at 3:1.

<sup>a</sup> Conversion of aryl bromides and yields of product from GC analysis.

only Pd/LDH-F catalyst is valuable for catalyst recycling in the Heck reaction.

### 3.5. Catalyst recycling

For practical application in the Heck reaction, the lifetime of the heterogeneous catalysts and their reusability are very important factors. After the completion of the reaction, the catalysts were recovered by simple filtration and subsequently washed with water followed by dichloromethane, and reused in the Heck reaction of bromobenzene with styrene as presented in Table 5. From therein it can be seen that only Pd/LDH-F catalyst was undergone to recycle without significant loss in catalytic activity. The catalyst was recycled up to four times, and the yield of 81% was still achieved in the reaction. The activities of other two catalysts were obviously decreased in the reuse. Such as catalyst Pd/KF- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the yield was decreased from 67% to 25% after the 1st run. It is proposed that the decrease of the activity may be due to the loss of fluoride ions in the support. The potassium fluoride in the KF- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the analogues are easily lost after washing. However, the fluorine is retained by hydrotalcite because it is exchanged and is not simply physical adsorption, the fluoride anions could be immobilized firmly in the LDH-F support. The amounts of Pd leaching into solution were determined over Pd/LDH-F catalyst as the following: 0.90% (after 1st run) and 1.10% (after 2nd run) of total Pd content, respectively. These data indicate the Pd leaching is fairly low on Pd/LDH-F catalyst, which provide an important factor for the catalyst recycling. Meanwhile the catalyst Pd/LDH-F still retained well-crystallized hydrotalcites structure after reuse as presented in Fig. 1. Therefore, the catalyst Pd/LDH-F could be reused albeit

Table 5  
A comparison of different catalysts recycling in the Heck reaction

Catalyst	All yields <sup>a</sup> (%)			
	1st run	2nd run	3rd run	4th run
Pd/LDH-F	86	84	79	81
Pd/KF- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	67	25	15	11
Pd/KF-silica	65	33	18	13

Reaction conditions: bromobenzene (1 equiv.), styrene (1.4 equiv.), sodium acetate as base (1.1 equiv.), 0.1 mol% Pd, DMF as solvent, 140 °C, 12 h, nitrogen atmosphere. The Mg:Al ratio of LDH-F is 3:1.

<sup>a</sup> Conversion of aryl bromides and yields of product from GC analysis.

low leaching and was able to remain catalytic activity in the Heck reaction.

## 4. Conclusions

For the first time, the palladium supported on LDH-F hydrotalcite catalyst was developed and used for the Heck reaction of aryl bromides with styrene to exhibit higher activity and selectivity. The Mg:Al ratio of 3:1 is suitable for the hydrotalcite as support. Small amounts (0.1 mol% of Pd) of Pd/LDH-F catalyst are required to perform the Heck reaction of bromobenzene and styrene with high yield (86%) and selectivity (1:2:3 = 0:97:3) in the absence of any ligands. It is attributed to the presence of the high polarized basic fluoride ions in the support. Moreover, fluorine is retained in hydrotalcite structure because it is exchanged and is not simply physical adsorption. The catalyst Pd/LDH-F can be simply separated from the reaction mixture and reused after washing without significant loss in catalytic activity in the Heck reaction.

## Acknowledgment

We are grateful for the financial support of the National Natural Science Foundation of China (no. 20476092).

## References

- [1] R.F. Heck, J.P. Nolley, *J. Org. Chem.* 37 (1972) 2320–2322.
- [2] I.P. Beletskaya, A.V. Cheprakov, *Chem. Rev.* 100 (2000) 3009–3066.
- [3] A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A* 173 (2001) 249–274.
- [4] D. Morales-Morales, C. Grause, K. Kasaoka, R. Redon, R.E. Cramer, C.M. Jensen, *Inorg. Chim. Acta.* 300–302 (2000) 958–963.
- [5] M. van der Boom, D. Mikstein, *Chem. Rev.* 103 (2003) 1759–1792.
- [6] A. Ehrentraut, A. Zapf, M. Beller, *Synletters* (2000) 1589–1592.
- [7] A.F. Littke, G.C. Fu, *J. Am. Chem. Soc.* 123 (2001) 6989–7000.
- [8] R.G. Heidenreich, J.G.E. Krauter, J. Pietsch, K. Köhler, *J. Mol. Catal. A* 182–183 (2002) 499–509.
- [9] S. Mukhopadhyay, G. Rothenberg, A. Joshi, M. Baidossi, Y. Sasson, *Adv. Synth. Catal.* 344 (2002) 348–354.
- [10] B. Pawelec, R. Mariscal, J.L.G. Fierro, *Appl. Catal. A* 225 (2002) 223–237.
- [11] S.H. Choi, J.S. Lee, *J. Catal.* 193 (2000) 176–185.
- [12] S.S. Pröckl, W. Kleist, M.A. Gruber, K. Köhler, *Angew. Chem. Int. Ed.* 43 (2004) 1881–1882.
- [13] C.P. Mehnert, J.Y. Ying, *Chem. Commun.* (1997) 2215–2216.
- [14] C.P. Mehnert, D.W. Weaver, J.Y. Ying, *J. Am. Chem. Soc.* 120 (1998) 12289–12296.

- [15] M.R. Buchmeiser, K. Wurst, *J. Am. Chem. Soc.* 121 (1999) 11101–11107.
- [16] M.R. Buchmeiser, T. Schareina, R. Kempe, K. Wurst, *J. Organomet. Chem.* 634 (2001) 39–46.
- [17] A. Corma, H. Garcia, A. Leyva, A. Primo, *Appl. Catal. A* 247 (2003) 41–49.
- [18] T.H. Bennur, A. Ramani, R. Bal, B.M. Chanda, S. Sivasanker, *Catal. Commun.* 3 (2002) 493–496.
- [19] S.V. Ley, C. Ramarao, R.S. Gordon, A.B. Holmes, A.J. Morrison, I.F. McConvey, I.M. Shirley, S.C. Smith, M.D. Smith, *Chem. Commun.* (2002) 1134–1135.
- [20] K. Kaneda, M. Higuchi, T. Imanaka, *J. Mol. Catal.* 63 (1990) L33–L39.
- [21] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* 124 (2002) 14127–14136.
- [22] B. Basu, P. Das, M.M.H. Bhuiyan, S. Jha, *Tetrahedron Lett.* 44 (2003) 3817–3820.
- [23] B.M. Choudary, M.L. Kantam, V. Neeraja, K.K. Rao, F. Figueras, L. Delmotte, *Green Chem.* 3 (2001) 257–260.
- [24] Z. Marczenko, *Spectrophotometric Determination of Elements*, Ellis Horwood Limited, Chichester, UK, 1976.
- [25] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* 11 (1991) 173–301.