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Communication

Preparation of palladium nanoparticle catalyst in ionic liquid and its catalytic properties for Heck-Mizoroki reaction

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ABSTRACT

A palladium nanoparticle (PdNPs) catalyst was synthesized in halogen-free anion ionic liquid (1-butyl-3-methylimidazolium lactate, [Bmim]Lac) by a simple chemical approach. The transmission electron microscopy analysis confirmed the presence of highly dispersed PdNPs in [Bmim]Lac with small average particle size distribution from 2.2 to 3.1 nm. The size of the PdNPs increases with decreasing molar ratio of [Bmim]Lac to Pd(OAc)₂ and increasing temperature. The activity of PdNPs@[Bmim]Lac catalyst was tested by the Heck-Mizoroki reaction, and the conditions were optimized. The catalyst can efficiently catalyze couplings of various aryl bromides and iodides with different olefins, giving good yields of products under the optimal conditions and be recycled up to six consecutive times.

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The Pd-catalyzed Heck-Mizoroki reaction has been extensively used to prepare functional materials, natural products, and bioactive compounds [1]. Homogeneous Pd catalysts with high activity are traditionally used, but they are difficult to recycle and dispose of on a large scale, have high toxicity, and are expensive [2]. Reusable and sustainable heterogeneous catalysts such as ligand-free Pd catalysts [3,4] have been extensively investigated as an alternative. The use of ionic liquids (ILs) containing imidazolium cations has attracted particular attention [5].

ILs stabilize metal nanoparticles (NPs) and prevent them from becoming inactive [6]. Heterogeneous nanocatalysts stabilized by ILs composed of halogen-free anions are desirable from an environmental perspective [7]. An IL coupled to a lactate anion is reusable, non-toxic, and environmentally benign [8], and we envision that the hydroxyl and carboxyl groups of the lactate stabilize the PdNPs by interacting with the metal

surface. Herein, we report the preparation of a PdNP catalyst stabilized by 1-butyl-3-methylimidazolium lactate (PdNPs@[Bmim]Lac) and its use in the Heck-Mizoroki reaction.

The PdNPs@[Bmim]Lac catalyst was prepared by stirring Pd(OAc)₂ (0.05 mmol) and [Bmim]Lac (1 mmol) in methanol (10 mL). The color changed from pale yellow to black indicating formation of PdNPs. UV-Vis absorption spectra of the Pd species before and after reduction were measured at $\lambda = 300$ and 800 nm, respectively. The characteristic absorption band for Pd(II) is at 380 nm. Its disappearance indicated that Pd(0) had formed [9]. The reducing agent is usually methanol, but to establish if the lactate anion participates in this reduction, electrospray ionization mass spectrometry (ESI-MS) was carried out. This was done at the end of the reaction, however, pyruvate anions (formed from oxidation of the lactate) were not detected.

The effect of the molar ratio of [Bmim]Lac to Pd(OAc)₂ and

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Fig. 1. TEM images of the PdNPs@[Bmim]Lac at different molar ratios of [Bmim]Lac/Pd(OAc)₂. (a) 10:1 at r.t.; (b) 20:1 at r.t.; (c) 30:1 at r.t.; (d) 20:1 at 45 °C; (e) 20:1 at 65 °C; (f) 20:1 at r.t. after six cycles.

the temperature on the size of the PdNPs was examined (Fig. 1 and Table 1). The catalytic activity was assessed using the Heck-Mizoroki reaction with 4-iodoanisole and styrene (Table 1). Transmission electron microscopy (TEM) results showed that when the molar ratio of [Bmim]Lac/Pd(OAc)₂ was increased from 10:1 to 20:1 the size of the PdNPs decreased from 2.7 to 2.3 nm (Fig. 1(a) and (b)). The PdNP size decreased from 2.3 to 2.2 nm as the molar ratio went from 20:1 to 30:1 (Fig. 1(b) and (c)). We propose that the [Bmim]Lac IL is involved in both dispersing and stabilizing the PdNPs. A layer of ions forms around the Pd atom and provides the necessary electrostatic and steric stabilization. Immediate formation of a surrounding stable layer occurs as the PdNPs grow.

The size of PdNPs increased as the temperature increased

Table 1

The effect of PdNP size on the Heck-Mizoroki reaction.

$\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{I} + \text{CH}_2=\text{CH}-\text{C}_6\text{H}_5 \xrightarrow[\text{Et}_3\text{N, DMF/H}_2\text{O (4:1)}]{\text{Pd cat., 90 }^\circ\text{C}} \text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$					
Entry	[Bmim]Lac/Pd(OAc) ₂ (mol/mol)	<i>t</i> /°C	Time (h)	Average size (nm)	Yield ^a (%)
1	10:1	r.t.	6	2.7	80
2	20:1	r.t.	6	2.3	84
3	30:1	r.t.	6	2.2	85
4	20:1	45	1	2.9	79
5	20:1	65	0.5	3.1	77

Reaction conditions: 4-iodoanisole (1.0 mmol), styrene (1.5 mmol), Et₃N (3.0 mmol), DMF/H₂O (4:1, 6.0 mL) and catalyst (1 mol% Pd) at 90 °C for 9 h. ^a Determined by GC analysis with hexamethylbenzene as the internal standard.

(Fig. 1(b), (d), and (e)). The higher temperature caused the additional nuclei to form quickly, and their deposition on the

Table 2

Optimization of the Heck-Mizoroki reaction conditions.

$\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{I} + \text{CH}_2=\text{CH}-\text{C}_6\text{H}_5 \xrightarrow[\text{base, solvent}]{\text{Pd cat., heating}} \text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$					
Entry	Base	Solvent (vol/vol)	[Pd] (mol%)	<i>t</i> /°C	Yield ^a (%)
1	Et ₃ N	toluene	2.0	90	12
2	Et ₃ N	EtOH	2.0	90	27
3	Et ₃ N	i-PrOH	2.0	90	30
4	Et ₃ N	DMF	2.0	90	39
5	Et ₃ N	DMF/H ₂ O (4:1)	2.0	90	92
6	Et ₃ N	H ₂ O	2.0	90	20
7	Na ₂ CO ₃	DMF/H ₂ O (4:1)	2.0	90	60
8	NaOH	DMF/H ₂ O (4:1)	2.0	90	62
9	K ₂ CO ₃	DMF/H ₂ O (4:1)	2.0	90	65
10	Na ₃ PO ₄ ·12H ₂ O	DMF/H ₂ O (4:1)	2.0	90	87
11	Et ₃ N	DMF/H ₂ O (5:1)	2.0	90	89
12	Et ₃ N	DMF/H ₂ O (3:1)	2.0	90	86
13	Et ₃ N	DMF/H ₂ O (2:1)	2.0	90	78
14	Et ₃ N	DMF/H ₂ O (4:1)	2.0	80	75
15	Et ₃ N	DMF/H ₂ O (4:1)	2.0	100	91
16	Et ₃ N	DMF/H ₂ O (4:1)	2.0	110	88
17	Et ₃ N	DMF/H ₂ O (4:1)	—	90	0
18	Et ₃ N	DMF/H ₂ O (4:1)	0.5	90	47
19	Et ₃ N	DMF/H ₂ O (4:1)	1.0	90	84
20	Et ₃ N	DMF/H ₂ O (4:1)	1.5	90	89
21	Et ₃ N	DMF/H ₂ O (4:1)	3.0	90	92

Reaction conditions: 4-iodoanisole (1.0 mmol), styrene (1.5 mmol), base (3.0 mmol), solvent (6.0 mL) for 9 h. ^a Determined by GC analysis (hexamethylbenzene as an internal standard).

existing particles induced the further growth of PdNPs. The size of PdNPs had an effect on the Heck-Mizoroki reaction (Table 1). A higher yield was observed when a smaller PdNP was used. This is because of the larger specific surface area providing more active sites. The preparation conditions of the catalysts were [Bmim]Lac/Pd(OAc)₂ (20:1) and r.t. in the following study.

The coupling of 4-iodoanisole with styrene was selected as a model reaction and the conditions were optimized (Table 2). Anhydrous toluene, EtOH, *i*-PrOH, or DMF (*N,N*-dimethylformamide) gave low yields of less than 40% at 90 °C (Table 2, entries 1–4). When an organic/aqueous co-solvent system (DMF/H₂O) was used the yield increased to 92% (Table 2, entry 5). This may be because [Bmim]Lac has good dispersion in

H₂O. When H₂O alone was used as the solvent, a low yield was observed (Table 2, entry 6) possibly because of poor substrate solubility. Different bases were then screened, and Et₃N gave the best result (Table 2, entries 7–10). This corresponds to results reported in the literature [10,11]. We infer that Et₃N has a positive influence on the reaction rate and the catalyst stability as that of tetrabutylammonium bromide (TBAB) reported [12]. In addition, stabilization of the catalytic system with ammonium salts extends the palladacycle life [13]. Different volume ratios of DMF to H₂O were investigated (Table 2, entries 11–13), and the volume ratio of 4:1 is still the best. Similar to literature reported, a temperature of 90 °C was found to be the optimum (Table 2, entries 14–16) [14]. The coupling reaction does not proceed in the absence of the Pd catalyst (Table 2,

Table 3

Scope of the Heck-Mizoroki reaction.

$\text{R}_1\text{-C}_6\text{H}_4\text{-X} + \text{CH}_2=\text{CH-R}_2 \xrightarrow[\text{Et}_3\text{N, DMF/H}_2\text{O (4:1)}]{\text{Pd cat., 90 }^\circ\text{C}} \text{R}_1\text{-C}_6\text{H}_4\text{-CH=CH-R}_2$						
Entry	X	R ₁	R ₂	Time (h)	Yield ^a (%)	Product
1	I	4-OCH ₃		9	92	
2	I	4-CH ₃		9	93	
3	I	4-NO ₂		9	82	
4	I	H		9	92	
5	Br	4-CHO		9	92	
6	Br	4-CN		9	93	
7	Br	4-OCH ₃		9	91	
8	Br	4-NO ₂		9	75	
9	Br	2-OCH ₃		11	60	
10	I	4-OCH ₃	COOCH ₃	8	93	
11	I	4-OCH ₃	COOC ₄ H ₉	9	91	
12	I	4-OCH ₃	COOH	7	92	
13	I	4-CH ₃	COOC ₄ H ₉	10	87	
14	I	4-CH ₃	COOH	7	96	
15 ^b	Cl	H		24	<5	
16 ^b	Cl	4-OCH ₃		24	<5	
17 ^b	Cl	4-NO ₂		24	<5	

Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), Et₃N (3.0 mmol), DMF/H₂O (4:1; 6.0 mL) and catalyst (2 mol% of Pd) at 90 °C.

^a Isolated yield for *trans* product. ^b Determined by GC analysis with hexamethylbenzene as an internal standard.

entry 17). The yield increased as the amount of PdNPs increased with a peak at 2.0 mol% PdNPs (Table 2, entry 5). To summarize, the optimal conditions are 1.0 mmol aryl halide, 1.5 mmol olefin, 2.0 mol% PdNPs@[Bmim]Lac, 3.0 mmol Et₃N, and 6.0 mL DMF/H₂O (4:1) at 90 °C.

The substrate scope of the Heck-Mizoroki reaction was tested with a variety of aryl halides and olefins under the optimized conditions (Table 3). Aryl bromides and iodides substituted with electron-withdrawing (–NO₂, –CN, –CHO) and electron-donating groups (–OCH₃, –CH₃) are tolerated and give the corresponding products in high yield (Table 3, entries 1–9). Notably, the aryl bromide and iodide with an –NO₂ group gave a lower yield than with the –OCH₃ group (Table 3, entry 1 vs entry 3; entry 7 vs entry 8). A similar result has been observed in the literature [15]. The lower yield and longer reaction time observed for the *O*-methoxy analogue may be attributed to steric hindrance (Table 3, entry 9). Again, a similar result has been reported in the literature [16]. Olefins such as acrylic acid and methyl- or butyl-acrylate were very well tolerated. The larger the geometrical size of acrylate ester, requires a longer reaction time (C₄H₉>CH₃>H) (Table 3, entries 10–14). Aryl chlorides give low yields of product with a long reaction time (Table 3, entries 15–17). Thus, the PdNPs@[Bmim]Lac catalyst exhibits good functional group tolerance and high catalytic activity. We infer that [Bmim]Lac and Et₃N jointly contribute to the stability and activity of the PdNP catalyst. Formation of PdNPs surrounded by lactate anions provide a coulombic barrier for collisions and stop clusters growing into the metal. In addition, the carboxyl and hydroxyl groups of the lactate may provide sufficient stabilization and disperse the PdNPs.

The reusability of the PdNP catalyst (1 mol% of Pd) was investigated. After one cycle the products were extracted with diethyl ether and the solvents and Et₃N were removed with a rotary evaporator. The catalyst was then used for up to 6 more experiments (Fig. 2). TEM results showed that the average particle size of PdNP increased from 2.3 to 5.0 nm (Fig. 1(f)). This observation may be attributed to the Ostwald ripening process.

Fig. 2. Recycling tests for the standard reaction. Reaction conditions: 4-iodoanisole (1.0 mmol), styrene (1.5 mmol), catalyst (1 mol% of Pd), Et₃N (3.0 mmol), and DMF/H₂O = 4:1 (6.0 mL) at 90 °C for 9 h.

Atomic absorption spectroscopy (AAS) showed that approximately 0.3% of the total Pd remains in the ether extract. This Pd sample was tested in the coupling of 4-iodoanisole and styrene under the optimized conditions and did not exhibit catalytic activity.

In conclusion, we have reported the simple and reproducible preparation of the PdNPs@[Bmim]Lac catalyst using a non-toxic and environmentally benign lactate anion IL as the stabilizer. TEM confirmed the presence of highly dispersed PdNPs in the [Bmim]Lac with an average particle size of 2.2–3.1 nm. This catalyst efficiently catalyzes the Heck-Mizoroki reaction for a range of aryl bromides and iodides with different olefins and can be recycled up to six consecutive times.

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Graphical Abstract

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Preparation of palladium nanoparticle catalyst in ionic liquid and its catalytic properties for Heck-Mizoroki reaction

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A PdNPs@[Bmim]Lac catalyst was prepared using a non-toxic and environmentally benign lactate anion IL as a stabilizer. The catalyst can be used efficiently for the Heck-Mizoroki reaction of various aryl halides with different olefins and can be reused.

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绿色离子液体中纳米钯催化剂的制备及其催化Heck-Mizoroki反应性能

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摘要: 发展了在非卤素绿色离子液体1-丁基-3-甲基咪唑离子液体乳酸盐中制备纳米Pd催化剂的简便化学方法. 透射电镜结果表明, Pd纳米粒子高度分散在[Bmim]Lac离子液体中, 平均粒径为2.2–3.1 nm. Pd纳米粒子的大小随着体系中[Bmim]Lac与Pd(OAc)₂摩尔比减小和温度升高而增大. 考察了离子液体稳定纳米Pd催化剂(PdNPs@[Bmim]Lac)催化Heck-Mizoroki反应性能, 并对反应条件进行了优化. 结果表明, 所制备的离子液体稳定的纳米Pd催化剂在优化条件下可高效催化系列卤代芳烃与烯烃的Heck-Mizoroki反应, 且可循环使用6次.

关键词: 钯纳米粒子; Heck-Mizoroki反应; 1-丁基-3-甲基咪唑离子液体乳酸盐; 绿色离子液体

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钯催化的Heck-Mizoroki反应广泛应用于制备功能材料、天然产物和生物活性物质的中间体^[1]. 该反应经常采用均相Pd基催化剂, 存在催化剂分离回收困难、有毒、价格昂贵和废弃物处理等问题^[2]. 因此, 可持续重复使用的非均相催化剂如无配位体的Pd催化剂广受关注^[3,4], 特别是在含咪唑阳离子的离子液体领域^[5].

离子液体能够稳定金属纳米粒子, 避免纳米粒子形成团聚而失活^[6]. 从环保角度出发, 开发新型不含卤素阴离子的离子液体稳定纳米催化剂具有重要意义^[7]. 含乳酸阴离子的离子液体具有可再生、无毒和环境友好等特性^[8], 我们设想乳酸盐阴离子中含有的羟基和羧基具备与金属表面相互作用的可能而进一步稳定金属纳米颗粒. 在此, 我们报道了一种利用1-丁基-3-甲基咪唑乳酸盐离子液体稳定Pd纳米颗粒(PdNPs@[Bmim]Lac)的催化剂的制备方法及其在Heck-Mizoroki反应中的催化性能.

将Pd(OAc)₂ (0.05 mmol), [Bmim]Lac (1 mmol)及甲醇(10 mL)混合并搅拌一定时间. 混合物的颜色由亮黄色变为黑色表明形成了Pd纳米粒子. 还原过程中Pd(II)的还原程度利用紫外-可见吸收光谱($\lambda = 300\text{--}800\text{ nm}$)进行检

测. 由于Pd(II)在380 nm处有特征吸收峰, 该峰消失表明Pd(II)完全还原为Pd(0)^[9]. 甲醇通常用作Pd(II)还原为Pd(0)的还原剂. 为了考察乳酸根阴离子是否参与该还原过程, 我们用ESI-MS检测还原后混合物, 未发现乳酸根阴离子被氧化的产物丙酮酸根阴离子. 这说明在制备催化剂过程中乳酸根阴离子很稳定, 没有参与Pd(II)的还原.

考察了[Bmim]Lac与Pd(OAc)₂的摩尔比和制备温度对所形成Pd纳米粒子的影响(图1和表1), 并测试了所制催化剂对4-碘苯甲醚与苯乙烯Heck-Mizoroki反应的催化性能. 由图1可见, Pd纳米粒子的粒径随着[Bmim]Lac用量增加而减小, 与纳米颗粒大小随稳定剂用量增加而减小的规律一致. 当[Bmim]Lac/Pd(OAc)₂摩尔比从10:1升至20:1时, Pd纳米粒子的平均粒径从2.7 nm降至2.3 nm(图1(a)和(b)); 当该摩尔比继续升至30:1时, Pd纳米粒子的平均粒径从2.3 nm略降到2.2 nm(图1(b)和(c)). 我们认为, [Bmim]Lac离子液体在反应体系中具有分散和稳定Pd纳米粒子的作用, 可在Pd纳米粒子周围形成提供位阻和电阻保护的离子层. 当Pd纳米粒子长大后, 在它周围迅速形成稳定层.

另外, Pd纳米粒子的粒径随着温度升高而增大(图1(b), (d)和(e)). 这是因为Pd纳米粒子在第一次成核后, 较高温下, 其他核的形成及其与前驱体的共沉积(在已形成的核上)速率较快, 导致Pd纳米粒子快速生长而长大. 由表1可见, Pd粒子越小, 产物产率越高, 这是因为在Pd用量相同时, 平均粒径越小的Pd纳米颗粒体系可提供更多的活性中心. 因此, 下文采用粒径较小的催化剂(图1(b)).

以4-碘苯甲醚和苯乙烯的偶联作为模型反应优化了反应条件(表2). 溶剂和碱是影响反应结果的重要因素. 在90 °C下, 当使用无水溶剂如甲苯、乙醇、异丙醇和*N,N*-二甲基甲酰胺(DMF)时, 产物产率小于40%(表2, 实验1–4), 当使用有机溶剂和水的混合溶剂时, 如DMF/H₂O, 目标产物的产率可达92%(表2, 实验5). 这可能是因为[Bmim]Lac离子液体与水有良好的互溶性, 离子液体稳定的纳米催化剂体系可高度分散. 然而, 仅仅用水作为溶剂时产率很低(表2, 实验6), 可能是因为反应底物在水中溶解度很小的缘故. 当对碱进行优化时, 发现Et₃N用作碱最佳(表2, 实验7–10), 与文献结果一致^[10,11]. 此外, 有研究表明, 四丁基溴化铵(TBAB)对该类偶联反应的反应速率及催化剂的稳定性有促进作用^[12]; Herrmann等^[13]也发现, 使用铵盐可延长Pd催化剂的使用寿命. 本文研究结果发现, 以Et₃N为碱, DMF与H₂O体积比为4:1, 在90 °C时, 该催化体系效率最高(表2, 实验11–16). 温度影响反应的变化规律与文献相同^[14]. 我们还考察了催化剂使用量对反应的影响(表2, 实验17–21). 结果发现, 不加Pd催化剂, 偶联反应则不能进行(表2, 实验17); 随着催化剂使用量增加, 产物产率逐渐增加, 至2 mol%时最高(表2, 实验5). 因此, 最佳反应条件为: 1.0 mmol芳基卤, 1.5 mmol烯烃, 2.0 mol% PdNPs@[Bmim]Lac, 3.0 mmol Et₃N和6.0 mL DMF/H₂O(4:1), 温度为90 °C.

基于以上研究结果, 我们对PdNPs@[Bmim]Lac催化芳基卤与烯烃发生Heck-Mizoroki反应的底物范围进行了拓展(表3). 结果表明, 该催化剂对一系列具有不同官能团的底物具有普适性. 即含吸电子基(–NO₂, –CN,

–CHO)、电中性基团(H)或供电子基团(–OCH₃, –CH₃)的溴苯和碘苯能与苯乙烯高效偶联, 目标产物的产率较高(表3, 实验1–9). 含供电子基团–OCH₃的反应物的偶联效率较含吸电子基团–NO₂的溴苯和碘苯更高(表3, 实验1和3, 7和8), 与文献结果一致^[15]. 此外, 我们发现, 邻甲氧基溴苯的活性较低, 这是因为邻位基团空间位阻较强的缘故(表3, 实验9), 与文献^[16]结果相似. 此外, 含供电子基团(–OCH₃, –CH₃)的碘苯能高效地与丙烯酸、丙烯酸甲基和丙烯酸丁酯偶联. 对丙烯酸酯化合物而言, 随着取代基碳数的增加, 获得接近目标化合物产率的反应时间增加(表3, 实验10–14). 当以芳基氯化物为反应底物时, 产物产率小于5%(表3, 实验15–17). 由此可见, PdNPs@[Bmim]Lac催化剂对反应底物的官能团具有较好的普适性. 我们推断, [Bmim]Lac与Et₃N的协同有助于提高催化剂的稳定性及活性. 围绕在Pd纳米粒子周围的乳酸阴离子对纳米粒子碰撞形成库仑屏障, 阻碍Pd金属簇的进一步团聚. 此外, 通过提供孤对电子, 乳酸阴离子中的羧基和羟基均能进一步促进Pd纳米粒子的稳定性.

图2考察了4-碘苯甲醚与苯乙烯Heck-Mizoroki反应中催化剂的重复使用性能, 催化剂Pd的使用量为1 mol%. 在反应结束后, 反应产物可以用乙醚完全萃取. 将残留物旋蒸去除溶剂及Et₃N后, 所得PdNPs@[Bmim]Lac催化剂直接用于下一次反应. 由图2可见, 催化剂可循环使用6次. TEM结果显示, 使用6次后, Pd纳米粒子的粒径从原来的2.3 nm增至5.0 nm(图1(f)), 这可能是因为奥斯特瓦尔德熟化过程所致. 原子吸收光谱测定表明在乙醚萃取液中含有0.3%的Pd. 旋转蒸发除去乙醚后, 在相同条件下进行反应, 所流失的Pd几乎没有催化作用.

总之, 我们采用自然、可再生、无毒和对环境友好的乳酸阴离子离子液体制备了PdNPs@[Bmim]Lac催化剂, 方法简单. Pd纳米粒子高度分散在[Bmim]Lac中, 平均粒径为2.2–3.1 nm. 催化剂可高效催化一系列芳基溴化物和碘化物与不同烯烃的Heck-Mizoroki反应, 且可循环使用6次.