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Palladium Complexes Immobilized on FSM-16 as Catalysts for Heck Reaction

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Palladium complexes immobilized on pyridine-carboimine and quinoline-carboimine functionalized FSM-16 were prepared by following reactions: (1) surface modification of FSM-16 with 3-aminopropyl group *via* silylation; (2) preparation of corresponding carboimine functionalized FSM-16 by reaction of pyridinecarboaldehyde and quinolinecarboaldehyde with 3-aminopropylated FSM-16; (3) formation of complex with $PdCl_2$. The Pd-complexes were characterized by XRD, N_2-adsorption, FT-IR, ICP and TG analyses and tested as potential catalysts in Heck vinylation of aryl halides with methyl acrylate. These catalysts were found to be active in Heck vinylation of aryl iodides and activated aryl bromides with conversion of 100 % in 1-5 h. Selectivity to *trans*-stereoisomer more than 99 % has been achieved. In case of less reactive aryl bromides, addition of quaternary ammonium salt increased activity of catalysts, but significant leaching of palladium into solution has been observed. These immobilized catalysts can be easily separated from reaction mixture by filtering and re-used for further reaction.

Key words: Palladium-carboimine complex; immobilization; ordered mesoporous silica; FSM-16; Heck vinylation

1. INTRODUCTION

Heck-type reactions, such as Heck vinylation and Suzuki coupling, *etc*., are one of the most important C-C coupling reactions in organic synthesis. They are mostly catalyzed in solution by palladium species generated from either Pd (0) compounds or Pd (II) salts [1]. Sometimes, homogeneous Pd catalysts precipitate from the solution and oxides to lose catalytic activity. Moreover, recovery or recycling of an active homogeneous Pd catalyst is difficult.

The heterogenization of homogeneous catalysts can help to overcome these problems. Palladium supported on carbon [2,], metal oxides [3], mesoporous silica [4] and zeolites [5-7] was found to be suitable catalyst for Heck reactions of aryl iodides and activated bromides in polar solvents. Nevertheless, deactivation of the catalyst by leaching of the palladium into solution under reaction conditions is the major drawback of these catalysts due to ability of polar solvent to remove Pd colloids from support and stabilize them in solution [8,9].

The immobilization of palladium complexes on organic and inorganic supports has been shown an efficient method to avoid palladium leaching. Moreover, nitrogen chelating ligands have been found an effective replacement of phosphine ligands in Heck type reactions. In addition, these ligands are air stable, cheap and nontoxic. The amino-functionalized silica supported palladium catalysts [10] or palladium complexes immobilized on silica functionalized with chelating nitrogen ligands [11] have been successfully tested in Heck reaction of iodobenzene with ethyl acrylate and styrene as active and stable catalysts. Clark et al. [12] have reported C-C coupling using pyridinium palladium complexes immobilized on MCM-41.

We report the preparation and characterization of palladium complexes immobilized on pyridine-carboimine and quinoline-carboimine functionalized mesoporous FSM-16. These complexes were tested in Heck vinylation of aryl halides with methyl acrylate catalytically active and re-usable catalysts.

2. EXPERIMENTAL

2.1. Catalyst preparation

FSM-16 vacuum dried at 250 °C for 1 h (1.0 g) was suspended in anhydrous toluene (30 ml). Then 1.35 mmol of 3-aminopropyltrimethoxysilane was added and the mixture was stirred under reflux for 2 h. Toluene containing methanol was distilled off, next portion of toluene (10 ml) was added and the reflux was continued for another 0.5 h. 3-Aminopropylated FSM-16 was recovered by filtration, washed with toluene and dried at 40 °C overnight.

Reaction of 2-pyridinecarboaldehyde with 3-aminopropylated FSM-16 was performed as follows: 1.35 mmol of 2-pyridinecarboaldehyde was added to 3-aminopropylated FSM-16 (1.0 g) in ethanol followed by stirring at room temperature for 24 h under nitrogen atmosphere. The pyridine-carboimine functionalized FSM-16 was filtered off, washed with ethanol and dried at 40 °C overnight. The same procedure was applied for 2-quinolinecarboaldehyde.

The complexation of functionalized FSM-16 was performed with $PdCl_2$. An appropriate amount of $PdCl_2$ was dissolved in acetone. One drop of conc. HCl was added to improve solubility of $PdCl_2$. Then, functionalized FSM-16 was replaced to prepared solution. The suspension was maintained for 4 h with stirring at room temperature. The physisorbed complex was removed by extraction with refluxing in dichloromethane for 5h.

The Pd immobilized catalysts were characterized by X-ray diffraction (XRD), sorption measurement, FT-IR spectroscopy, ICP, and TG analyses. XRD spectra were recorded on a Shimadzu XRD-6000 spectrometer with Cu Kα radiation (λ = 1.5418 Å). Nitrogen isotherms were obtained using a Belsorp 28SA apparatus (Bel Japan, Osaka, Japan) at −196 °C. TG/DTA measurements were performed on a Shimadzu DTG-50 analyzer. Formation of C=N double bond in functionalized FSM-16 after addition of ligands was confirmed by FT-IR spectroscopy using Thermo Nicolet Nexus 470 by KBr technique. Amount of Pd in catalysts was determined by ICP (JICP-PS-1000UV, Leeman Labs, Tokyo, Japan).

2.2. Reaction and analysis

In a typical Heck-vinylation reaction, aryl halide (2 mmol), methyl acrylate (5 mmol), base (2 mmol), solvent (5 ml) and catalyst (0.2 mol% of Pd) were taken in a round bottom flask. The mixture was degassed by argon flow followed by heating at 130 °C for required time. Reaction mixture was analyzed by GC (Shimadzu GC-14A equipped with 25 m capillary column Ultra-1 and a FID detector) and products were characterized by GC-MS (Shimadzu GCMS-QP500, the same conditions as used in GC).

In recycling studies, the catalyst was separated from reaction mixture by filtration, washed with solvent and then with dichloromethane to remove organic compounds. After drying at 90 °C, it was re-used.

3. RESULTS AND DISCUSSION

3.1. Characterization of catalyst

XRD patterns of calcined FSM-16, Pd complex immobilized on pyridine-carboimine (Pd-2PC) and quinoline-carboimine (Pd-2QC) functionalized FSM-16 are shown in Figure 1.

The X-ray diffraction pattern for pure FSM-16 shows characteristic low-angle peaks attributed to d_{100}, d_{110} and d_{200} reflections assuming a hexagonal lattice [13]. As for the Pd-2PC and Pd-2QC catalysts, there is no essential change in XRD patterns compared with that of FSM-16. Thus, immobilization of palladium complexes on FSM-16 did not affect structure of ordered silica. The physico-chemical properties of catalysts are listed in Table I.

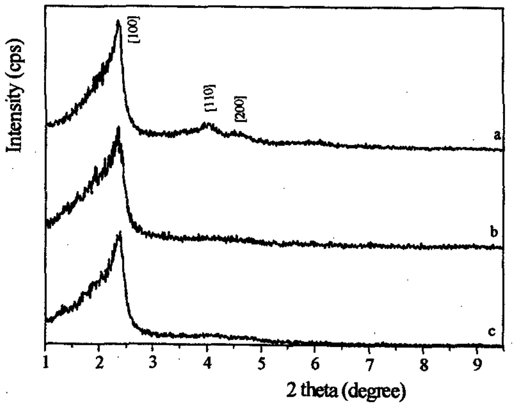


Fig. 1. XRD patterns for FSM-16 (a), Pd-2PC (b) and Pd-2QC (c).

Table I. Physico-chemical properties of catalysts.

Catalyst	Surface area[a] ($m^2.g^{-1}$)	Ligand[b] ($mmol.g^{-1}$)	Pd[c] (wt.%)
FSM-16	997	-	-
Pd-2PC-FSM	456	1.08	1.9
Pd-2QC-FSM	420	0.99	2.2

[a] BET method, [b] TG analysis, [c] ICP

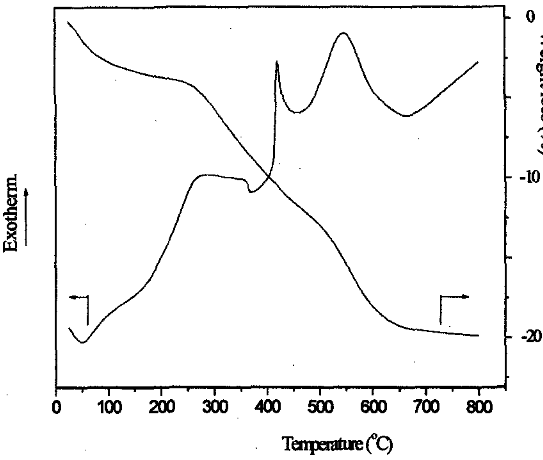


Fig. 2. TG-DTA profile of 2QC-FSM

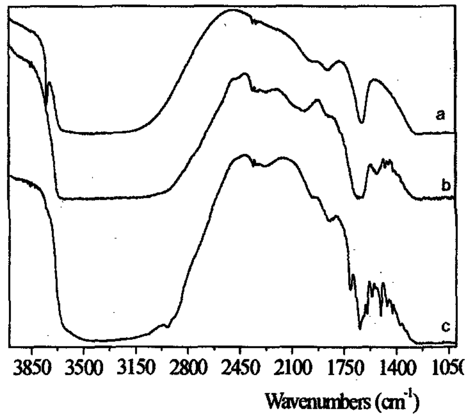


Fig. 3. FT-IR spectra in region of 4000-1000 cm^{-1} of FSM-16 (a) (peaks at 3476, 1625 cm^{-1}), AP-FSM (b) (peaks at 1635, 1527, 1474, 1448 cm^{-1}) and functionalized 2QC-FSM (c) (peaks at 1706, 1646, 1598, 1563, 1506 and 1430 cm^{-1})

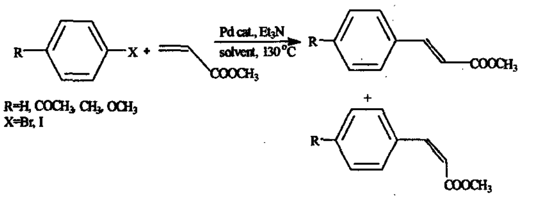
TG-DTA was used to determine the amount of ligand incorporated to aminopropylated FSM-16 (2PC and 2QC). TG-DTA profile of 2QC is shown in Figure 2. The mass loss is mainly divided into three temperatures regions: below 150 °C, 150-620 °C and above 620 °C. Weight loss of sample during heating from 25 to 150 °C corresponds to loss of loosely bound water (3.7 %). Large weight loss of around 16-19 % at temperature between 470-620 °C is due to decomposition of covalently bonded organics. Similar result was obtained for 2PC. In Figure 3, a comparison is made among

FSM-16, 3-aminopropylated FSM-16, and functionalized FSM-16 with 2-quinolinecarboaldehyde in the range of 4000-1000 cm^{-1}.

FT-IR spectra of freshly calcined FSM-16 (Fig. 3a) have characteristic adsorption band at 3746 cm^{-1}, which is attributable to the OH stretching vibrations of isolated (single) silanol groups, a band at 1625 cm^{-1} is assigned to OH bending vibration of adsorbed water. After 3-aminopropylation reaction of calcined FSM-16 with 3-aminopropyltrimethoxysilane, series of peaks at 1450-1530 cm^{-1} in FT-IR spectra of 3-aminopropylated FSM-16 (Fig. 3b) are due to C-H stretching of the hydrocarbon chain (ν_{CH2}). No peak assigned to amino group (ν_{NH2}) can not be observed in spectra of 3-aminopropylated FSM-16 due to small number densities of amines in the material. On the contrary, imines have strong bands that are easy to identify by infrared spectroscopy. Formation of quinoline-carboimine bases by reaction of 3-aminopropylated sample with 2-quinolinecarboaldehyde is demonstrated by the presence of the adsorption peak at 1646 cm^{-1} (Fig.4 c) due to the C=N double bond. The shoulder at 1706 cm^{-1} is probably due to adsorbed unreacted aldehyde. Sharp peaks at 1600-1500 cm^{-1} correspond to C=C stretching in quinoline.

3.2. Heck reaction

Palladium-complexes immobilized on ordered silica were tested in Heck vinylation of aryl halides with methyl acrylate (Scheme 1) in polar and non-polar solvents using triethylamine as base.



Scheme 1. Heck vinylation by palladium complexes immobilized on FSM-16.

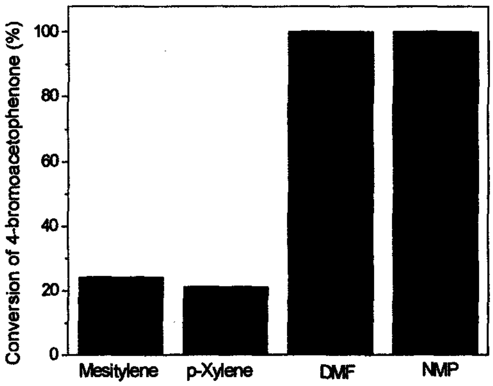


Fig. 4. Conversion of 4-bromoacetophenone in polar and non-polar solvents. Reaction conditions: 130 °C, catalyst (Pd-2QC) 0.2 mol%, base: Et_3N, 2 mmol, solvent 5 ml, period: 24 h.

Polar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), acetonitrile or *N*-methylpyrrolidone (NMP) are commonly used for homogeneous Heck reaction. They provide high rates due to stabilization of active Pd species by forming shell of coordinating solvent molecules around clusters [14]. Efficiency of polar solvents in comparison with non-polar was confirmed in Heck vinylation of 4-bromoacetophenone (Fig. 4). Conversion of 4-bromoacetophenone 100 % has been achieved in polar solvents (DMF, NMP) in 2 h. In case of non-polar solvents (mesitylene, *p*-xylene), even the increase of reaction time to 48 h did not result in the increase of 4-bromoacetophenone conversion (*ca* 20 % conversion). Conversion of aryl iodides and aryl bromides in Heck reaction with methyl acrylate over Pd-2QC and Pd-2PC catalysts is listed in Table II. Both catalysts were found to be active for aryl iodides and activated aryl bromides with 100 % conversion in 1-5 h and the products of the vinylation were highly selective (99 % for *trans*-isomer). Aryl bromides with electron-donating substituents ($-OCH_3$, $-CH_3$, -H) were found to be particularly sluggish in their activity (entries 5, 8, 10) with 10-30 % conversion after 24 h. This trend is in agreement with the order of reactivity for aryl bromides in homogeneous catalysis [1].

Table II. Heck vinylation of aryl halides with methyl acrylate over Pd-2QC and Pd-2PC catalysts[a].

No	Substrate	Pd (mol%)	Additive	Time (h)	Conversion (%)	
					Pd-2QC	Pd-2PC
1	4-Iodoanisole	0.1	-	1	100	100
2	4-Iodotoluene	0.1	-	1	100	100
3	4-Bromonitrobenzene	0.1	-	1	95	90
4	4-Bromoacetophenone	0.1	-	1	51	46
5	Bromobenzene	0.2	-	24	32	30
6	Bromobenzene	0.2	Bu_4NBr	17	63	65
7	Bromobenzene[b]	0.2	Bu_4NBr	17	<1	-
8	4-Bromotoluene	0.2		24	30	29
9	4-Bromotoluene	0.2	Bu_4NBr	17	68	63
10	4-Bromoanisole	0.2		24	19	13
11	4-Bromoanisole	0.2	Bu_4NBr	17	50	50

[a] Reaction conditions: aryl halide, 2 mmol; methyl acrylate, 2 mmol; catalyst, (Pd against halide); Et_3N 2 mmol; solvent, NMP; temperature, 130 °C, Bu_4NBr 15 mol.%. [b] Conversion of bromobenzene in second cycle.

Table III. Catalytic activity of Pd-2QC in Heck vinylation of bromobenzene with methyl acrylate.[a]

Solvent system	Pd (mol%)	Bu_4NBr (mol%)	Conv. (%)
Toluene	0.2	15	4.5
	0.2	60	22.8
	0.2	100	21.7
	0.52	100	42.3
	0.52	100	0.5[b]
H_2O-Toluene(1:5)	0.2	30	0
H_2O	0.2	15	0
1,4-Dioxane	0.2	15	3.6

[a] Reaction conditions: 130 °C, Et_3N 2.5 mmol, bromobenzene 2 mmol, methyl acrylate 5 mmol, catalyst Pd-2QC.[b] Conversion of bromobenzene in second cycle.

The rate of reaction of less reactive aryl bromides can be improved by addition of *tetra*-butylammonium bromide (Table II, entries 6, 9 and 11). Bu_4NBr used as an additive (15 mol.% based on aryl bromide) in Heck vinylation of aryl bromides with electron donating substituents increased reaction rate and yield of desired products very effectively (yield of coupling products 50-70 % was obtained after 17 h reaction). Such increase of the activity by adding Bu_4NBr is due to leaching of palladium to the solution. In a leaching experiment, after taking hot filtrate at 16 % conversion of bromobenzene after 30 min, the reaction then, continued during further 3 h. The conversion after 3 h reaction 38 % in the filtrate indicates that significant amount of palladium reacts in homogeneous phase. Moreover, in second cycle, only very less formation of methyl cinnamate was observed (Table II, entry 7). The possibility of using other solvent system has been investigated to suppress palladium leaching by the addition of quaternary ammonium salt.

Results of Heck vinylation of bromobenzene with methyl acrylate in various solvents using Bu_4NBr as additive are given in Table III. Low catalytic activity of Pd-2QC in other solvents was obtained under same conditions used for NMP as solvent. An increase of the amount of Bu_4NBr to the stoichiometric compared with the amount of bromobenzene, together with the increase of the catalyst concentration to 0.52 mol% of Pd led to significant increase of the conversion (42 %) in toluene (Table III). However, no activity of catalyst in the second cycle (0.5 % conv.) in toluene suggests that this increase of activity is accompanied by leaching of palladium into solution by the addition of Bu_4NBr. These results show that Bu_4NBr enhances the leaching of palladium species from palladium complexes immobilized on functionalized FSM-16.

Palladium complexes immobilized on FSM-16 have shown high catalytic activity in recycling experiments (Table IV) in Heck reaction of 4-bromoacetophenone with methyl acrylate. After the separation from reaction mixture by filtration, they were re-used in seven reaction cycles without loss of the activity.

Table IV. Recycling and re-use of Pd-2QC and Pd-2PC in reaction of 4-bromoacetophenone with methyl acrylate [a]

	Conversion in cycle (%)						
Ligand	1	2	3	4	5	6	7
2QC	99	99	99	99	99	98	97
2PC	93	94	93	92	91	93	91

[a] Reaction conditions: 4-bromoacetophenone, 2mmol; methyl acrylate, 2 mmol; temperature, 130 °C; catalyst, 0.1 mol %; Et_3N, 2 mmol; NMP, 5 ml; period, 10 h.

4. CONCLUSIONS

Palladium immobilized on pyridine-carboimine and quinoline-carboimine functionalized ordered mesoporous FSM-16 were found to be active and selective catalysts for the Heck vinylation of aryl iodides and activated aryl bromides with methyl acrylate These heterogenized catalysts were easily separated from reaction mixture by filtration. More than seven reaction cycles can be performed without significant loss of activity over both 2-QC and 2-PC catalysts. In the case of less reactive aryl bromides, the addition of the quaternary ammonium salt increased catalytic activity, but significant leaching of palladium to the solution has been observed.

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