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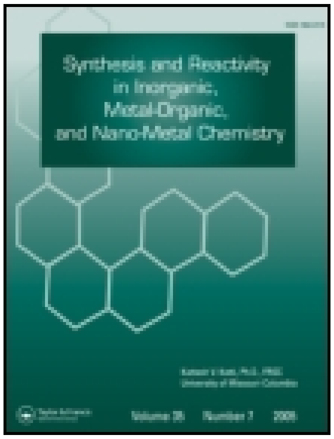

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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In Situ Generation of Supported Nano-Palladium on La_2O_3: An Efficient and Recyclable Catalyst for Heck Cross-Coupling Reaction

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In Situ Generation of Supported Nano-Palladium on La_2O_3: An Efficient and Recyclable Catalyst for Heck Cross-Coupling Reaction

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The Pd/La_2O_3 catalyst was simply prepared from readily available reagents. The catalyst exhibited high activities in the Heck cross-coupling reaction and could be reused for several times without activity loss. In addition, the catalyst was characterized by the transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and inductively coupled plasma (ICP).

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Keywords catalyst, Heck reaction, La_2O_3, nano-palladium

INTRODUCTION

The palladium-catalyzed Heck cross-coupling reaction between aryl halides and alkenes is a very convenient and excellent method for the formation carbon–carbon bonds at unsubstituted vinylic positions.[1,2] This reaction has been used in the pharmaceutical industry for the synthesis biologically active compounds, natural product, and conjugated polymers. In the past few years, the Heck reaction catalyzed by palladium complexes along with phosphine ligands in homogeneous system has made great progress. However, as with all homogeneous catalysts, there is separation, recovery, reuse of expensive palladium catalysts, and reduction of palladium contamination of the isolated products problems. These problems are of environmental and economic concern for the pharmaceutical industry where large volumes of hazardous wastes and high production costs are of great importance. To overcome these problems as previously mentioned, palladium complexes, which are the most popular catalysts in the Heck reaction, have been immobilized on various supports,[3–5] used in ionic liquids,[6,7] and microencapsulated in polymeric coating.[8,9]

Generally, these heterogeneous Pd catalyst systems exhibit high catalytic activity and selectivity in the Heck reaction. However, they are not always as reactive as homogeneous catalysts with ligands. In view of the practical and industrial applications, the developing a ligandless, recyclable new heterogeneous catalyst system to dispense with the use of expensive, toxic, air-sensitive ligands for the Heck reactions catalyzed by palladium catalysts is highly desirable. Basic metal oxide La_2O_3 as preferred promoters has been widely reported.[10,11] However, its use as a support for catalytic applications is not well explored in the Heck reaction. In this respect, we report for the first time the Heck reaction of aryl halides on heterogeneous palladium nanoparticles directly supported basic metal oxide La_2O_3.

EXPERIMENTAL

Materials and Physical Measurements

La_2O_3 support was prepared through the precipitation method of $La(NO_3)_3$ with $NH_3{\cdot}H_2O$ at pH 10.5, followed by recovery of the solid powder with filtration, washing, drying and then calcinations at 500°C. $PdCl_2$ (AR) was obtained from Shanghai July Chemical Co. Ltd. (China) and used as received. Solvents were obtained from Sinopharm Chemical Reagent Co. Ltd (China) and purified prior to use. Other chemicals were purchased from Sigma-Aldrich (China) or Alfa Aesar (China) and used without further purification or drying. Containing 2 wt% Pd/La_2O_3 catalyst was prepared by the modification of a literature preparation of Pd/TiO_2[12]: impregnation of the La_2O_3 powder using a 0.1 M acidified solution of $PdCl_2$, then the sample was evaporated, dried, and calcined in air at 500°C for 3 h.

X-ray photoelectron spectroscopy (XPS) measurements were analyzed on coated alumina with a physical electronics PHI-Quantum 2000 Scanning ESCA Microprobe (Physical Electronics Company, USA) with Al Kα radiation. Inductively coupled plasma (ICP) analyses were performed on an Ultima 2 analyzer (Jobin Yvon, France). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max RA diffractometer (Japan)

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with Cu Kα radiation. Morphology of catalyst was analyzed on a JEOL 2010 transmission electron microscope (TEM, Japan). GC analysis was measured by a Varian 430 Gas Chromatograph (USA) using a column packed with DC-200 stationary phase. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer (Germany) using $CDCl_3$ as solvent.

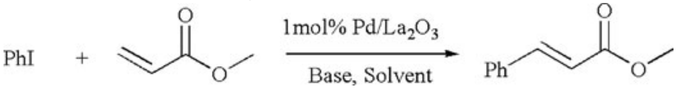
Typical Heck Reaction

Iodobenzene (0.2 mmol), methyl acrylate (0.3 mmol), sodium acetate (0.3 mmol), Pd/La_2O_3 (1 mol%), and DMA 2 mL were added to a 25 mL flask equipped with a magnetic stirring bar under nitrogen atmosphere. The reaction mixture was stirred at 120°C for 10 h. After the reaction, the reaction mixture was cooled to room temperature, separated, and purified by column chromatography (SiO_2, ethyl acetate/hexane). Unless otherwise stated, product yields from the Heck reaction were determined by column chromatography. The product was dried under vacuum, weighted, and characterized by NMR spectroscopy.

RESULTS AND DISCUSSION

In order to investigate the catalytic property of the 2 wt% Pd/La_2O_3 catalyst, Heck reaction of the cross-coupling of methyl acrylate with iodobenzene was employed. In the Heck reaction, the base was used to neutralize the acid ensuing from the exchange of a hydrogen atom with an aryl group. The change of product yield with different base under the same conditions (120°C, 10 h) is shown in Table 1. When inorganic base NaOH was used in the reaction, it provided a poor yield (17%) (entry 1). The higher product yields (65%, 75%) were obtained with the aid of K_3PO_4, K_2CO_3 (entries 2 and 3). Compared with the previous base, the catalytic activity of the system greatly increased with the use of NaOAc as a base (entry 5). When the organic base Et_3N was used in the reaction, a moderate yield (64%) was obtained. DMA was found to be more effective than other solvents such as DMF, DMSO, and NMP (entries 5–8). The oxidative conditions seriously inhibited the desired reaction, as indicated by the reaction performed under air or oxygen atmosphere (entries 9 and 10).

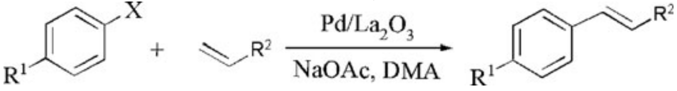
TABLE 1
Influence of various bases of the Heck reaction of iodobenzene with methyl acrylate in the presence of 2 wt% Pd/La_2O_3 as catalyst[a]



Entry	Base	Solvent	Yield (%)[b]
1	NaOH	DMA	17
2	K_3PO_4	DMA	65
3	K_2CO_3	DMA	75
4	Et_3N	DMA	64
5	NaOAc	DMA	97
6	NaOAc	DMF	87
7	NaOAc	NMP	85
8	NaOAc	DMSO	71
9[c]	NaOAc	DMA	23
10[d]	NaOAc	DMA	5

[a]Reaction conditions: 0.2 mmol PhI, 0.3 mmol methyl acrylate, 0.3 mmol base, 2 mL solvent, 1 mol% Pd/La_2O_3, 120°C, 10 h. [b]Isolated yield. [c]Under air. [d]Under O_2, GC yield.

TABLE 2
Heck reaction between aryl halides and alkenes in the presence 2 wt% Pd/La_2O_3 catalyst[a]



Entry	X	R^1	R^2	Time (h)	Temperature (°C)	Yield (%)
1	I	$COCH_3$	CO_2Me	10	120	93
2	I	H	CO_2Me	10	120	97
3	I	OCH_3	CO_2Me	10	120	85
4	Br	H	CO_2Me	24	140	80
5	Br	OCH_3	CO_2Me	24	140	56
6	Br	CH_3	CO_2Me	24	140	79
7	I	H	$CO_2{}^tBu$	10	120	90
8	I	H	Ph	10	120	87

[a]Reaction conditions: 0.2 mmol aryl halides, 0.3 mmol alkenes, 0.3 mmol NaOAc, 1 mmol% Pd/La_2O_3, 2 mL DMA; isolated yields; All the products were characterized by ^1H NMR and ^{13}C NMR.

We examined a wide array of aryl halides and alkenes to extend the scope of this catalytic system. The results are presented in Table 2, a range of aryl iodides and aryl bromides could undergo Heck reaction to produce exclusively *trans* products

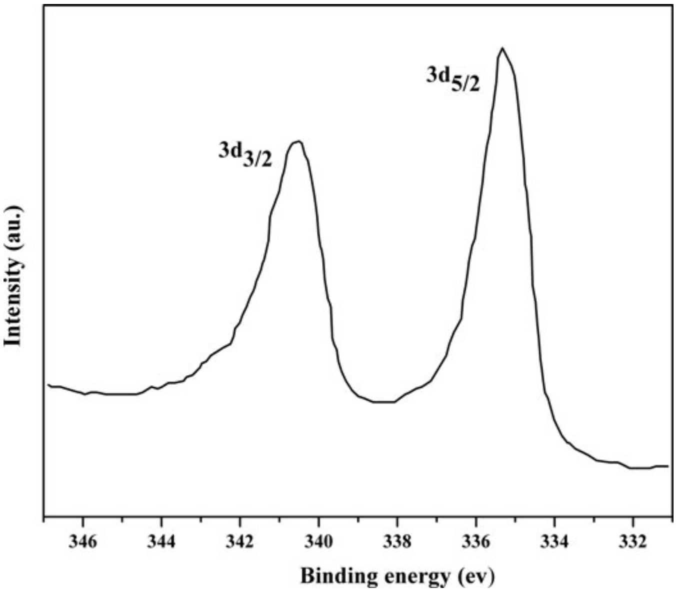


FIG. 1. XPS spectra of Pd/La_2O_3 catalyst after the first run.

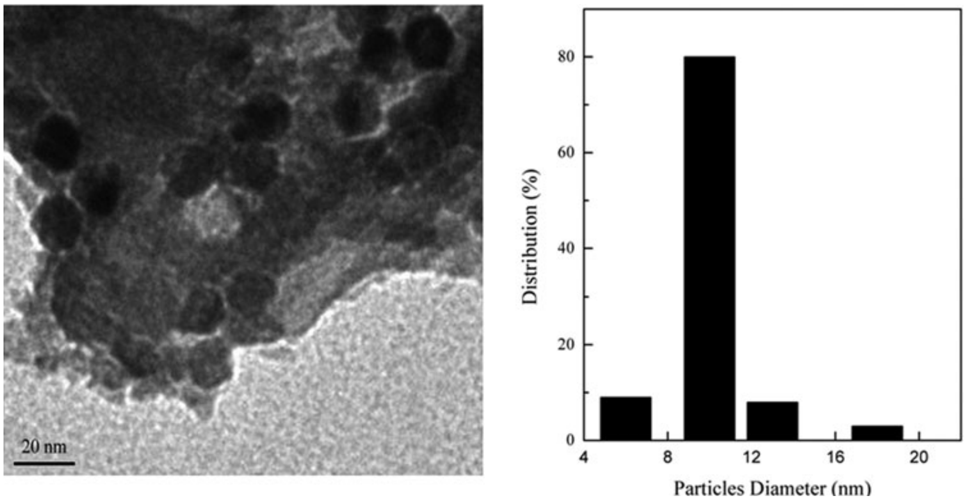


FIG. 2. TEM images of 2 wt% Pd/La_2O_3 catalyst after the first run and its statistics histogram.

in moderate to excellent yields. The best results were obtained in the reaction with the highly reactive aryl iodides. A slower reaction was observed with aryl bromides, but increasing the reaction time from 10 h to 24 h provided the desired product (entries 4, 5, 6). Furthermore, electron-rich 4-bromanisole could be coupled in moderate yield (entry 6). Concerning the variation of the alkenes, as expected, alkenes ($R^2 = CO_2{}^tBu$, Ph) also gave better yields (entries 7, 8).

XRD analysis indicated that the peaks from the fresh 2 wt% Pd/La_2O_3 solid sample catalyst and after the first run are similar in profile, and no palladium-containing species were observed due to low amount of Pd content or its high dispersion (S.1). Although no Pd species could be detected by XRD, the presence of Pd species in this solid sample was clearly evidenced by XPS. Figure 1 shows the XPS spectra of the region corresponding to the binding energy range of 331–347 eV, which included Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks. The peaks located around 335.2 eV and 340.7 eV were assigned to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ level in the Pd(0) metallic form in agreement with literature report.[13] Before reaction, no Pd particles could be discerned in the TEM images for the 2 wt% Pd/La_2O_3 solid sample, suggesting that Pd species was likely highly dispersed on the surface of La_2O_3. However, inspection of the TEM images of isolated 2 wt% Pd/La_2O_3 catalyst samples after the first run indicated the involvement of Pd nanoparticles. Figure 2 displays the TEM image and corresponding size distribution of the isolated catalyst. Evidently, highly dispersed spherical metallic Pd nanoparticles with the size of 10 nm on the La_2O_3 surface were observed.

Recyclability is an essential advantage of heterogeneous catalysts over homogeneous ones. Hence, we tested the recyclability of this catalyst in the Heck reaction of iodobenzene with methyl acrylate. After the washing, the powder was dried at 250°C under vacuum for 1 h. This recovered catalyst retained its original activity even in the third cycle under optimized conditions. To verify whether the activity is derived from Pd/La_2O_3 or leached Pd species, contrasting experiments have been investigated under the same conditions obtained from the filtrate and wash solution of catalyst. After similar purification processes, the products from Heck reactions were obtained in only *ca*. 5% isolated yield. Analysis of the final reaction mixtures for dissolved palladium showed that an extremely low amount of Pd (0.6 ppm) had leached during the reaction by ICP. These results clearly suggest the reaction approximately proceed in heterogeneous conditions during the reaction, although we can not rule out the homogeneous process.[14–16] At present, the true mechanism regarding our catalysts is still unclear and related studies are underway in our laboratory.

CONCLUSION

In summary, we have developed a simple and efficient method for recyclable Pd-supported basic La_2O_3 and demonstrated their activities in Heck cross-coupling reaction. This heterogeneous catalyst is stable and robustness in recycling without noticeable loss of activity.

SUPPLEMENTARY MATERIALS

Powder X-ray diffraction patterns of Pd/La_2O_3 catalyst.

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