Full Paper

Applied Organometallic Chemistry

Received: 14 June 2014 Revised: 31 July 2014 Accepted: 24 August 2014

(wileyonlinelibrary.com) DOI 10.1002/aoc.3221

Preparation of siloxene nanosheet-supported palladium as sustainable catalyst for Mizoroki–Heck reaction

Fei-Bao Zhang*, Su-Fang Lv, Jian-Xiong Jiang and Yong Ni*

Siloxene nanosheets were successfully modified with palladium nanoparticles by reducing palladium chloride with hydrazine hydrate. The palladium nanoparticles–siloxene nanosheets as a catalyst for the Mizoroki–Heck reaction exhibited high activity, recoverability and stability. The structural morphology of the catalyst was investigated using transmission electron microscopy. High efficiency of the catalyst was proved in the Mizoroki–Heck reaction after five catalytic recycles. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: siloxene nanosheets; Mizoroki–Heck; catalyst; silane coupling agent

Introduction

Siloxene nanosheets (SNS) have attracted increasing attention in fundamental chemistry and physics mainly for their electronic properties and photophysics properties arising from the graphene-like honeycomb lattice structure or buckled sheets.[1–4] SNS can be applied in photovoltaic cells, nonvolatile memory, lighting, ultrasonic generators and biosensors with solution processibility[5–13] because of their good chemical versatility and tunability. They might be promising candidates for a catalyst or a catalyst support due to the high specific surface area and surface tunability. Therefore, considering their low cost, large surface area, stability in air and ease of modification to load metal clusters, SNS may be a promising material for catalytic applications.[14–16] Recently, various organic reactions catalyzed by nanosheet-based nanomaterials have been reported.[17–20] However, there are few reports of metal–SNS hybrids, catalytic properties and catalyst supports of SNS.

In the work reported in this paper, we developed a simple procedure to generate SNS-supported Pd nanoparticles to be used as a sustainable heterogeneous Pd catalyst for Mizoroki–Heck reactions. The results were still promising after the catalyst was recycled for ten runs.

Experimental

Materials

$CaSi_2$ was purchased from Alfa Aesar China Chemical Co. Palladium chloride and hydrazinium hydrate were purchased from Aladdin China Chemical Co. All reagents were used without further purification.

Catalyst Preparation

Preparation of starting SNS ($Si_6H_3(OH)_3$)

$Si_6H_3(OH)_3$ was prepared according to a method reported in the literature.[21,22] A mixture of $CaSi_2$ (1 g, 10.4 mmol) and HCl (100 ml, 37%) was stirred at 273 K for 2 days under an argon atmosphere. The products were filtered and washed with methanol, followed by the residue being dried under vacuum for 2 days at 373 K to afford SNS (0.48 g, 80%) as a gray solid.

Synthesis of functionalized SNS (AS-SNS)

Approximately 1 g of (3-aminopropyl)triethoxysilane (APTS) was first dispersed in 500 ml of a mixture of water and ethanol (2:8 v/v). Around 200 mg of SNS was introduced to this mixture with ultrasonication for 1 h, and then the mixture was heated to 343 K in a water bath and refluxed for 4 h. The solid product was collected by centrifugation and washed three times using the same mixture of water–ethanol to remove the residual coupling agent. After vacuum drying overnight, the functionalized SNS (AS-SNS) were obtained.

Preparation of Pd/AS-SNS nanocomposites

First, ethanol solutions of AS-SNS were sonicated for 1 h in deionized water, and then a certain amount of $PdCl_2$ dissolved in acidified water (0.05 M HCl) was added at 323 K with magnetic stirring. Subsequently, hydrazinium hydrate was added and stirred for another 3 h. The composites were filtered using a Millipore membrane (nylon, 0.45 mm, 47 mm), washed with ethanol, dried under vacuum. They are denoted as Pd-ASSN-2.5 (400 mg, 2.5 wt% Pd, thermo-AAS analysis).

For comparison, Pd-ASSN-10 (10 wt%), Pd-ASSN-5 (5 wt%) and Pd-ASSN-1 (1 wt%) were also prepared according to the same procedure.

---

* *Correspondence to: Fei-Bao Zhang and Yong Ni, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China. E-mail: feibaozhang@126.com*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China

Catalytic Tests and Recycling

Aryl halide (0.5 mmol), ethyl acrylate (0.6 mmol), triethylamine (1.0 mmol) and Pd-ASSN-10 (0.005 mmol Pd) were placed in a Schlenk tube equipped with a magnetic stirring bar. DMF (2 ml) was added to the tube and the reaction mixture was stirred at 383 K under nitrogen atmosphere. The reaction was monitored using TLC. After complete consumption of the starting material, the reaction was stopped, cooled to room temperature, separated and purified using column chromatography with silica gel (SiO_2, ethyl acetate–hexane). The product was dried under vacuum, weighed and characterized using NMR spectroscopy. Product yields from the Heck reaction were determined using column chromatography. A similar procedure was employed for other reactions (Table 3).

To investigate catalyst recyclability, the reaction was repeated with 4-iodotoluene as the substrate on a 2.0 mmol scale maintaining the same conditions as described above, except using the recovered catalyst. After the reaction was completed, the solid particles were collected by centrifugation, washed with DMF, ethanol and water, and dried under vacuum. The dried catalyst was reused for further catalytic runs.

Characterization

^1H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance 400 instrument and chemical shifts were recorded downfield of tetramethylsilane. Transmission electron microscopy (TEM; Hitachi 600, Japan) was used to observe the morphology and degree of agglomeration. GC-MS analyses were performed using an Agilent 26890 N/59731 equipped with a DB-5 column (30 m × 2.5 mm × 0.25 μm).

Results and Discussion

According to the reported method,[21] the starting Weiss SNS, $Si_6H_3(OH)_3$, were prepared with Zintl phase $CaSi_2$, a layered material with Si corrugated (111) layers linked by Ca ions. The structure of the siloxene has been reported to consist of Si (111) layers terminated above and below by OH groups and H atoms.[1,21] Due to the surface OH groups present on the nanosheets, it is easy for SNS to readily agglomerate in organic solvent. Coupling agent molecules can be adsorbed on the surface of the nanosheets by their hydrophilic end and can react with the surface OH groups on the nanosheets (as shown in Scheme 1) The APTS coupling agent undergoes hydrolysis and the Si—OC_2H_5 group transforms into Si—OH. One Si—OH group of the coupling agent reacts with the hydroxyl groups of the siloxene surface and forms a covalent bond, and two other Si—OH groups either undergo a condensation reaction with further Si—OH or can be in a free state and form hydrogen bonds. When surface OH groups on nanosheets react with the APTS coupling agent, γ-aminopropyl functional groups are introduced onto the nanosheets and they produce a thin organic shell on the surface of the nanosheets which can interact with palladium and reduce the agglomeration of nanoparticles (Scheme 1).

TEM Analysis

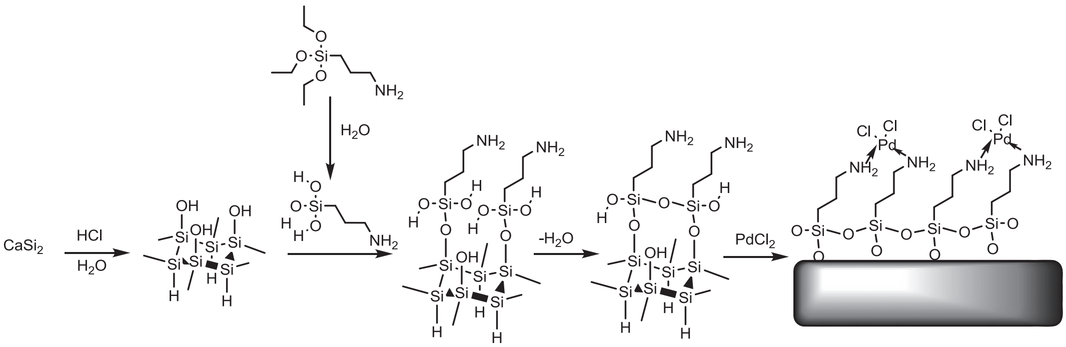
The morphologies of SNS and Pd/SNS composite were investigated using TEM (as shown in Fig. 1). Clearly, it can be seen that the sheets are almost transparent with flake-like shapes which indicates successful exfoliation, leading to an ultrathin morphology (Fig. 1(a)). AS-SNS shows no obvious difference in shape and structure from SNS (Fig. 1(b)). After surface functionalization via silylation of SNS with organosilane, the immobilized functional groups bonded onto the surface of SNS act as anchors for metal adsorption. Hydrophilic amino groups (—NH_2) show great affinity for the aqueous palladium chloride, and therefore facilitate the deposition of metal precursor and the formation of small and highly dispersed Pd nanoparticles on the nanosheets. From Fig. 1(c, d) it can be seen that Pd nanoparticles are well dispersed on the surface of SNS with a diameter of 2–5 nm. Size-similar and highly dispersed Pd nanoparticles can be synthesized easily with this method. For comparison, Pd nanoparticles supported on unmodified SNS were also prepared using a similar method, as shown in Fig. 1(e, f).

Catalytic Activity of Pd/SNS in Heck Coupling Reaction

The Heck coupling reaction was selected to evaluate the catalytic performance of the Pd-ASSN catalyst (Table 1). In our study, 4-iodotoluene with *n*-butyl acrylate was chosen as benchmark substrate in the coupling model reaction. Initially, the influence of various Pd metal concentrations on the coupling was investigated.

In the model reaction, catalysts of Pd supported on modified SNS (Table 1, entries 1–4), Pd supported on unmodified SNS (entry 5) and $Pd(OAc)_2$ (entry 6) were all tested under same reaction condition. Performing the reaction in the presence of Pd-ASSN-2.5 leads to a satisfactory yield of 95% (Table 1, entry 2).

In the Heck reaction, iodobenzene and *n*-butyl acrylate were initially selected as test substrate to examine the catalytic activity of the supported Pd materials. The reaction conditions were optimized, and the results are presented in Table 2. It is found that the best system for this reaction is DMF as solvent in combination with triethylamine as base, which gives a 99% conversion of iodobenzene at 90°C within 12 h (entry 5).



Scheme 1. Process of formation of Pd-ASSN composite materials.

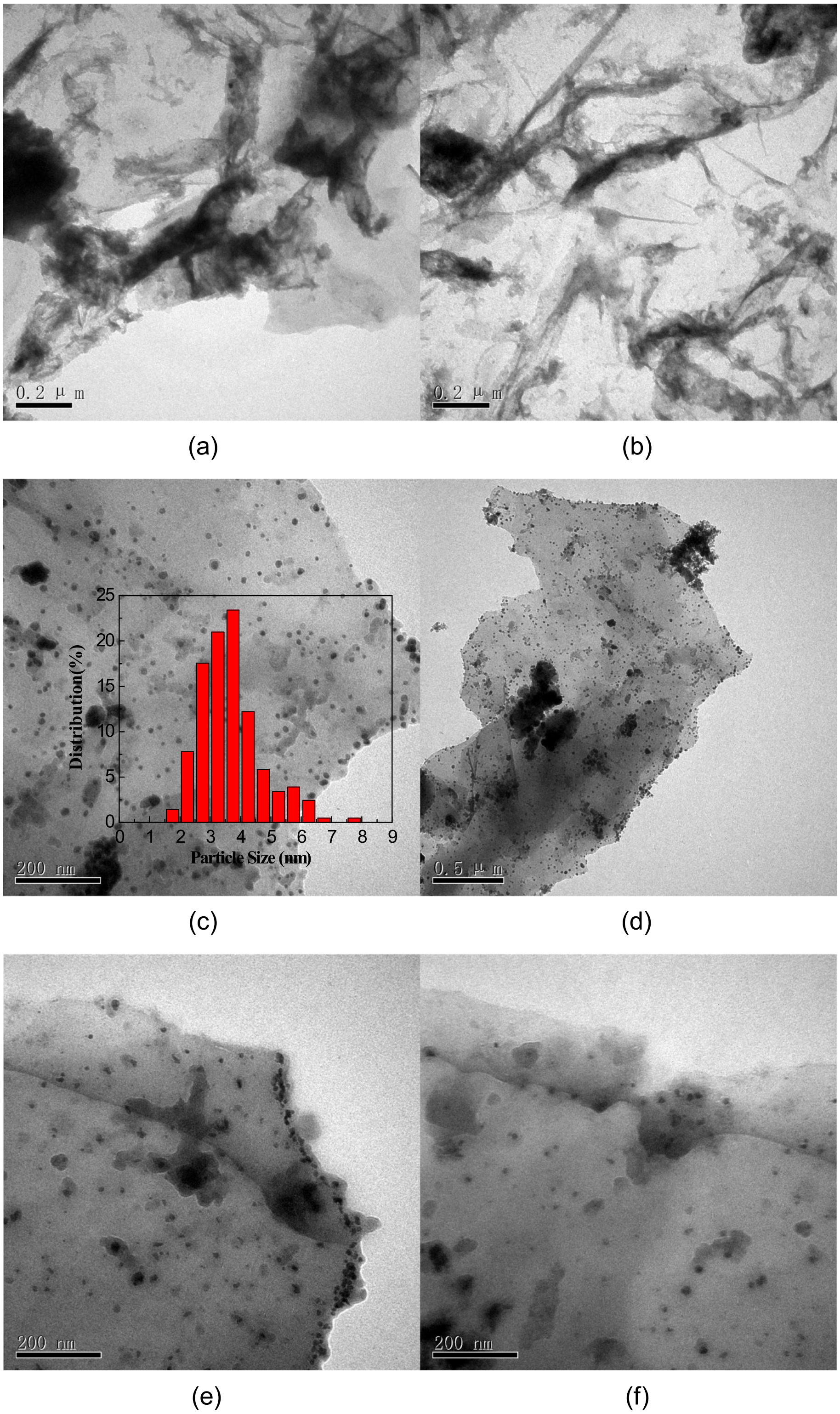


Figure 1. TEM images of as-prepared materials: (a) SNS; (b) AS-SNS; (c, d) Pd-ASSN-2.5 (inset in (c) shows a statistical size distribution of Pd nanoparticles); (e, f) Pd/SNS.

To generalize the application of the catalyst, the optimized conditions were employed in Heck reactions of *n*-butyl acrylate or styrene with various aryl halides (Table 3). The reactions proceed well with a wide range of aryl iodides and bromides with electron-donating and electron-withdrawing groups or without. For most cases, the reaction is completed in 12–32 h with good yields.

Catalyst Recovery and Heterogeneity Tests

Since the recyclability of a catalyst is very important for practical applications, the recovery and reusability of the catalyst under investigation were tested in the Heck reaction of iodobenzene with *n*-butyl acrylate under the optimized reaction conditions

Table 1. Various catalyst formulations in the model reaction of Heck coupling[a]

Entry	Catalyst	Pd (wt%)	Yield (%)[b]
1	Pd-ASSN-1	1	90
2	Pd-ASSN-2.5	2.5	95
3	Pd-ASSN-5	5	91
4	Pd-ASSN-10	10	89
5	Pd-SN-5	5	83
6	$Pd(OAc)_2$		72

[a] Reaction scale: 1 mmol of substrates.
[b] Determined using GC.

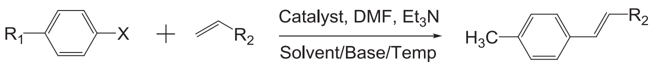
Table 2. Optimization of Heck coupling reaction in the presence of Pd-ASSN-5[a]

Entry	Solvent	Base	Temperature (°C)	Time (h)	Yield (%)[b]
1	DMF	NaAc	90	12	90
2	DMF	Na_2CO_3	90	12	95
3	DMF	*n*-Butylamine	90	12	78
4	DMF	Ethylenediamine	90	12	80
5	DMF	Triethylamine	90	12	≥99
6	H_2O	Triethylamine	90	12	—[c]
7	Ethanol	Triethylamine	90	12	65
8	Diethyl ether	Triethylamine	90	12	—[c]
9	THF	Triethylamine	90	12	—[c]
10	Acetone	Triethylamine	90	12	—[c]

[a] Reaction scale: 1 mmol of substrates.
[b] Determined using GC.
[c] No reaction.

Table 3. Catalytic performance of Pd-ASSN-5

Entry	X	R_1	R_2	Reaction time (h)	Reaction temperature (°C)	Yield (%)
1	I	H	$COOC_4H_9$	24	80	92
2	I	CH_3	$COOC_4H_9$	12	90	99
3	I	NO_2	$COOC_4H_9$	12	90	98
4	I	OCH_3	$COOC_4H_9$	24	90	88
5	Br	NO_2	$COOC_4H_9$	24	110	96
6	Br	CN	$COOC_4H_9$	24	110	75
7	Cl	H	$COOC_4H_9$	32	120	—
8	I	CH_3	Ph	32	90	92
9	I	NO_2	Ph	24	90	97
10	I	H	Ph	36	90	95
11	I	OCH_3	Ph	36	90	72
12	Br	NO_2	Ph	24	120	96
13	Br	CN	Ph	24	120	56



Scheme 2. Heck coupling reaction.

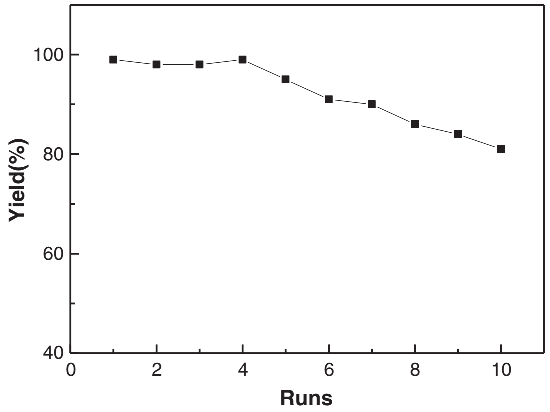


Figure 2. Long-term stability of Pd-ASSN-2.5 catalyst.

(Scheme 2). When the reaction was completed, the mixture was centrifuged and the liquid was poured out. The catalyst was collected and washed with acetone and ethanol, and dried under vacuum. Then, the recovered catalyst was reused in the same Heck reaction for ten runs. The catalyst maintained a high activity even in the fifth cycle under optimized conditions (95%). The results are shown in Fig. 2. Compared with the activity of Pd nanoparticles supported on other nanosheets,[23–25] the activity of Pd/SNS is not the highest. However, we find that the activity of Pd/SNS still remains high after ten catalytic cycles. Moreover, Pd/SNS is a cheap and easily obtained carrier. Therefore, we can foresee Pd/SNS being a promising catalyst support material.

Conclusions

We have introduced a new catalyst support of SNS obtained from the layered silicon compound $CaSi_2$. When modified using a silane coupling agent, palladium nanoparticles could be highly dispersed on the surface of the nanosheets, and the catalytic properties of the resulting material were tested in the Mizoroki–Heck reaction. High efficiency and stability of this catalytic system was shown for Heck coupling reactions with a number of aryl halides. This study suggests that SNS could be a promising support in heterogeneous catalysis.

Acknowledgements

This research was supported by Zhejiang Provincial Natural Science Foundation of China under Grant No. Y4100131 and the Scientific Research Fund of Dunhuang Academy under Grant No. 200808.

References

[1] H. Okamoto, Y. Sugiyama, H. Nakano, *Chem. Eur. J.* **2011**, *17*, 9864.
[2] B. K. Teo, X. H. Sun, *Chem. Rev.* **2007**, *107*, 1454.
[3] H. Nakano, M. Nakano, K. Nakanishi, D. Tanaka, Y. Sugiyama, T. Ikuno, H. Okamoto, T. Ohta, *J. Am. Chem. Soc.* **2012**, *134*, 5452.
[4] J. R. Dahn, B. M. Way, E. Fuller, *Phys. Rev. B* **1993**, *48*, 17872.
[5] Y. Sugiyama, H. Okamoto, T. Mitsuoka, T. Morikawa, K. Nakanishi, T. Ohta, H. Nakano, *J. Am. Chem. Soc.* **2010**, *132*, 5946.
[6] Z. C. Holman, C. Liu, U. R. Kortshagen, *Nano Lett.* **2010**, *10*, 2661.
[7] Y. Kumai, H. Kadoura, E. Sudo, M. Iwaki, H. Okamoto, Y. Sugiyama, H. Nakano, *J. Mater. Chem.* **2011**, *21*, 11941.
[8] S. G. Cloutier, P. A. Kossyrev, J. Xu, *Nat. Mater.* **2005**, *4*, 887.
[9] H. Rong, A. Liu, R. Jones, O. Cohen, D. Hak, R. Nicolaescu, A. Fang, M. Paniccia, *Nature* **2005**, *433*, 292.
[10] H. Okamoto, Y. Kumai, Y. Sugiyama, T. Mitsuoka, K. Nakanishi, T. Ohta, H. Nozaki, S. Yamaguchi, S. Shirai, H. Nakano, *J. Am. Chem. Soc.* **2010**, *132*, 2710.

[11] V. S. Y. Lin, K. Motesharei, K. S. Dancil, M. J. Sailor, M. R. Ghadiri, *Science* **1997**, *278*, 840.
[12] K. S. Dancil, D. P. Greiner, M. J. Sailor, *J. Am. Chem. Soc.* **1999**, *121*, 7925.
[13] M. J. S. Spencer, T. Morishita, M. Mikami, I. K. Snook, Y. Sugiyama, H. Nakano, *Phys. Chem. Chem. Phys.* **2011**, *13*, 15418.
[14] B. Basu, S. Paul, *Appl. Organometal. Chem.* **2013**, *27*, 588.
[15] Z. J. Wang, Q. Fu, X. H. Bao, *Prog. Chem.* **2014**, *26*, 506.
[16] F. Adam, J. N. Appaturi, A. Iqbal, *Catal. Today* **2012**, *190*, 2.
[17] S. J. Guo, S. J. Dong, *Chem. Soc. Rev.* **2011**, *40*, 2644.
[18] R. Mas-Balleste, C. Gomez-Navarro, J. Gomez-Herrero, F. Zamora, *Nanoscale* **2011**, *3*, 20.
[19] M. Osada, T. Sasaki, *Adv. Mater.* **2012**, *24*, 210.
[20] H. D. Velazquez, F. Verpoort, *Chem. Soc. Rev.* **2012**, *41*, 7032.
[21] H. Nakano, M. Ishii, H. Nakamura, *Chem. Commun.* **2005**, 2945.
[22] J. R. Dahn, B. M. Way, E. Fuller, *Phys. Rev. B* **1993**, *48*, 17874.
[23] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mulhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262.
[24] S. Ogasawara, S. Kato, *J. Am. Chem. Soc.* **2010**, *132*, 4608.
[25] K. Karami, M. Ghasemi, N. H. Naeini, *Catal. Commun.* **2013**, *38*, 10.