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Mercaptopropyl-Modified Mesoporous Silica: A Remarkable Support for the Preparation of a Reusable, Heterogeneous Palladium Catalyst for Coupling Reactions

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Abstract: The functionalization of SBA-15 with mercaptopropyl trimethoxysilane leads to a material capable of absorbing Pd from organic and aqueous solutions. The resulting Pd-loaded material acts as a catalyst for the Suzuki−Miyaura and Mizoroki−Heck coupling reactions. Leaching studies show that the filtrate contains as little as 3 ppb Pd after reaction. Aminopropylated silica is an effective scavenger, and catalyst for the Mizoroki−Heck reaction, but leaching is significant (35 ppm), illustrating the importance of the thiol ligand to retain Pd on the surface. Heterogeneity tests such as hot filtration experiments and three-phase tests show that the reaction is occurring predominantly via surface-bound Pd.

Introduction

Palladium-catalyzed reactions have become part of the standard repertoire of the synthetic organic chemist.[1] Coupling reactions such as the Mizoroki−Heck,[2] Suzuki−Miyaura,[3] and Buchwald−Hartwig[4] reactions provide one-step methods for assembling complex structures. Recent advances from the Fu group have allowed coupling reactions to be performed on previously unreactive aryl chlorides under mild conditions.[5] Palladium catalysts are also used routinely for hydrogenation and debenzylation reactions.

Despite the remarkable utility of Pd catalysts in organic synthesis, they suffer from one significant drawback, that they often remain in the organic products at the end of the reaction.[6] This is an extremely serious problem in the pharmaceutical industry because the level of heavy metals such as Pd in active pharmaceutical intermediates is closely regulated.

An obvious solution to the issue of Pd contamination is the substitution of heterogeneous catalysts for their homogeneous counterparts.[7,8] Palladium supported on materials such as carbon,[8b] ordered[8c,d] or amorphous silicates,[8e] and zeolites[8f] is commonly employed in catalysis.[8] Kobayashi has reported microencapsulated Pd in core−shell block copolymers,[9] and Pd catalysts have been immobilized on prefunctionalized surfaces displaying ligands such as phosphines,[10] carbenes,[11] pincer ligands,[12] and palladacycles,[13] to name a few. Alternatively, Pd recovery has been attempted by phase-segregation techniques employing soluble or thermomorphic polymers,[14] dendrimers,[15] fluorinated solvents,[16] supercritical carbon dioxide,[17] or ionic liquids.[18] Although these approaches do decrease the amount of Pd present in the product relative to homogeneous catlaysts, leaching of Pd from heterogeneous supports/ligands is fairly commonplace. There are an increasing number of cases in which it has been clearly demonstrated that heterogeneous catalysts are merely reservoirs for highly active soluble forms of Pd.[16,19]

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In several cases, it has been demonstrated that the metal can leach from the surface by interacting with the aryl halide substrate.[19b−d,20] Depending on the affinity of the product for Pd, reprecipitation of Pd on the surface generally occurs at the end of the reaction after the substrate has been consumed. Even ligand-functionalized surfaces are prone to leaching, which may be attributed to instability of the Pd-ligand bond or ligand-surface bond.[19] Ultimately the inherently higher catalytic activity of the trace amounts of soluble Pd, combined with weak ligation, is a major difficulty to be overcome in the area of supported catalysis.[21]

In the absence of truly effective supported catalysts, a variety of scavengers for Pd have been developed to treat the solution or substrate after the reaction. These are summarized in a recent comprehensive review by Prasad et al.[6a] and include three basic approaches: precipitation from solution after complexation by a ligand, adsorption onto a polymeric support which can be removed by filtration, or removal of the product while keeping Pd dissolved in solution. For example, palladium can be precipitated from solution using 2,4,6-trimercapto-*S*-triazine (TMT).[22] Treatment with unfunctionalized adsorbents such as charcoal is sometimes effective, but can also lead to significant losses of product which are also absorbed. Organic polymers functionalized with thiols such as MPTMT (mesoporous polystyrene bound TMT) and related species are commercially available, but require long reaction times in excess of 24 h and larges excesses of reagent to effectively remove Pd from solution.[23b] Interestingly, functionalized silica resins are reported to require decreased time for effective scavenging of Pd.[23c]

Inspired by the work of Fryxell et al.[24a] and Pinnavaia and Mercier,[24b] who demonstrated that thiol-modified mesoporous materials are remarkable scavengers for mercury, and by Kang et al.,[24c,d] who showed that SBA-15-SH has a higher affinity for Pd and Pt compared to other metals, we began a study of mercaptopropyl-modified SBA-15. We examined both the ability of this material to remove various forms of Pd from aqueous and organic solutions and, most importantly, the ability of the resulting material to actually catalyze coupling reactions.[25] Our hope was that the functionalized material would act both as a support and as a scavenger for any small amounts of residual Pd that escape from the surface.

We have found that not only is mercaptopropyl-modified SBA-15 a superb scavenger for Pd, but the resulting Pd-encapsulated material catalyzes the Mizoroki−Heck and Suzuki−Miyaura reactions, without leaching Pd into solution. At the end of the reaction, even using loadings as high as 2%, as little as 3 parts per billion Pd are observed in solution, accounting for only 0.001% of the initially added catalyst. Most remarkably, heterogeneity tests including hot filtration tests and three-phase tests have demonstrated that the catalysis occurs on the surface or in the pores of the silicate.

Results and Discussion

Synthesis of Functionalized Silicates. We chose to employ the mesoporous silicate SBA-15[26] as a support for the thiol ligands because it has high porosity, surface area, and high surface concentration of silanols. In addition, studies have shown that the thiol groups in large pore mesoporous materials are more accessible than those on amorphous silica,[27] although this may depend more on surface area and porosity than long-range order because disordered but highly porous organic inorganic composites also have high capacity for mercury scavenging.[28]

Two methods were employed to introduce the thiol groups. In the first approach, $(CH_3O)_3Si(CH_2)_3SH$ was reacted with a preformed silicate (SiO_2 or SBA-15). Functionalization of the surface occurred by condensation with surface silanols and loss of methanol leading to a loading of 2.2 mmol/g determined by elemental analysis. Additionally, a sol−gel synthesis in which the thiol ligand is incorporated directly into the material during its synthesis was also carried out according to Stucky's method.[29] Thus, $Si(OEt)_4$ and $(CH_3O)_3Si(CH_2)_3SH$ were added in a 94:6 molar ratio to a preformed solution of the polymeric surfactant in aqueous HCl.[29] After an appropriate reaction time (see Experimental Section), the surfactant was removed by extraction revealing the porous structure. In the sol−gel materials, a thiol loading of 6% or 1.0 mmol/g was generally employed, although materials with 8% and 10% loading were also prepared.[30] As a comparison, silica functionalized with mercaptopropyl groups was prepared by grafting mercaptopropyl trimethoxysilane on the surface of porous, amorphous silica.[31]

Scavenging Experiments. In an initial screen of silica-based adsorbents, we examined the ability of SBA-15-SH (prepared by grafting and sol−gel methods), amorphous silica (SiO_2-SH, grafted), SBA-15 itself, and Montmorillonite clay to remove $Pd(OAc)_2$ from THF (Figure 1) and $PdCl_2$ from water (Table 1). Montmorillonite clay and unfunctionalized SBA-15 were

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(31) The silica employed had a BET surface area of 297 m^2/g.

Figure 1. $Pd(OAc)_2$ in THF treated with various scavengers.

Table 1. Scavenging of Pd with SBA-15-SH and SiO_2-SH[a]

	after SBA-15-SH treatment		after SiO_2-SH treatment	
initial [Pd] (ppm)	[Pd] (ppm)	removed (%)	[Pd] (ppm)	removed (%)
2120	152	92.85	193	90.93
1590	111	93.05	142	91.10
1060	0.908	99.91	67.42	93.66
848	0.0052	99.9994	4.17	99.51
530	0.0011	99.9998	1.16	99.78
265	0.0005	99.99998		
106	0.00037	99.9996	0.0024	99.998

[a] Aqueous solutions of $PdCl_2$ (10 mL) treated with 100 mg of silicate for 1 h with stirring.

virtually ineffective. Amorphous silica functionalized with mercaptopropyl trimethoxysilane (SiO_2-SH) was the closest in effectiveness to SBA-15-SH, and thus the two were examined quantitatively by ICPMS (Table 1).

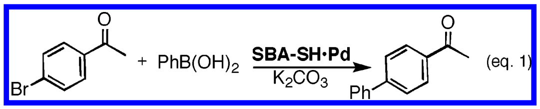
At high initial concentrations of Pd (1500−2000 ppm), ca. 93% of the added Pd was removed. At lower levels of initial contamination, more impressive results are obtained: a solution containing 1000 ppm of Pd can be reduced to less than 1 ppm of Pd with SBA-15-SH, which corresponds to removal of more than 99.9% of Pd. Treatment of the same solution with amorphous silica-SH leaves 67 ppm of Pd in solution, although certainly part of this difference can be attributed to the lower loading of thiol on amorphous silica (1.3 mmol/g) as compared to 2.2 mmol/g for SBA-15. Starting with a 500 ppm solution, treatment with SBA-**15**-SH gives a solution containing only 1.1 ppb Pd, corresponding to a 500 000-fold reduction in Pd content after one treatment, and removal of 99.9998% of the Pd in solution.

The material prepared by sol−gel incorporation of thiol behaved similarly to the grafted silicate, even though the loading of the thiol on support was 1.0 mmol/g rather than 2.2 mmol/g (grafted). Thus, scavenging an 848 ppm solution with the sol−gel material removed 99.991% of the Pd. At all loadings below this, more than 99.99% of the Pd was removed. Considering that the sol−gel material had one-half the thiol content of the grafted material, this is a remarkable result.

Finally, the ability of SBA-15-SH (grafted) and SiO_2-SH to scavenge selected Pd(II) and Pd(0) complexes in organic solvents was examined. In THF, the ordered and amorphous silicates were comparable, with the amorphous silicate having marginally greater capacity for Pd. Neither support was effective for the removal of $Pd(PPh_3)_4$.

Catalysis. We next examined the ability of the palladium-loaded silicates to actually catalyze coupling reactions.[8d,32] Much to our surprise, even materials with an excess of thiol on the support relative to Pd exhibited high catalytic activity for Suzuki−Miyaura and Mizoroki−Heck reactions of bromo and chloroaromatics. The catalyst prepared by sol−gel incorporation of the thiol[29] having a 4:1 S:Pd ratio was employed in catalytic runs (Table 2). Interestingly, functionalized silicates prepared by grafting the thiol on the surface of preformed SBA-15 were effective scavengers, but highly capricious catalysts. Out of 10 batches, only three displayed catalytic activity, with some being completely inactive. As a comparison, seven batches of material prepared by sol−gel incorporation were all active. The reasons for this are under investigation.

Table 2. Suzuki−Miyaura Couplings with SBA-SH-Pd[a]



entry	catalyst support	solvent[b]	conv. (yield)	Pd leaching (%, ppm)[c]	leaching of Si, S (ppm)
1	SBA-15	H_2O[d]	99 (98)	0.001, 0.003	n.d.[e]
2	SBA-15	H_2O[f]	97	0.04, 0.09	n.d.[e]
3[g]	SBA-15	DMF/H_2O	99	0.009, 0.02	n.d.[e]
4	SBA-15	H_2O	99 (97)	0.04, 0.09	168, 36
5[h]	SBA-15	H_2O	93 (80)	0.019, 0.08	108, 6
6	SBA-15	DMF	96 (94)	0.35, 0.75	14, 1.7
7	SiO_2	DMF	33 (31)	0.61, 1.30	20, 6.4
8	SiO_2	H_2O	99 (98)	0.39, 0.84	155, 17

[a] Unless otherwise noted, reaction conditions are 1% cat. 8 h, 80 °C. Conversions and yields are determined by GC versus internal standard unless otherwise noted. [b] DMF/H_2O in a 20/1 ratio. [c] As a % of the initially added Pd, and the ppm of the filtrate, determined by ICPMS. [d] 80 °C, 5 h. [e] Not determined. [f] 100 °C, 2 h. [g] Bromobenzene was used. [h] Chloroacetophenone was used with 2% cat., 24 h, 80 °C.

Reproducibly high catalytic activity was found in either DMF, water, or a mixture of the two solvents. Most notably, extremely low leaching of the catalyst is observed at the end of the reaction. In all cases, less than 1 ppm of Pd is present in the solution at the end of the reaction; in some cases, as little as 3 ppb Pd is observed, corresponding to a loss of only 0.001% of the initially added catalyst.[33]

The filtrate was also examined for the presence of silicon and sulfur. As shown in entries 4 and 5, both were observed for reactions run in water. However, in DMF, silicon and sulfur leaching was dramatically suppressed, but slightly higher Pd leaching was observed (0.35% of 1%, or 0.75 ppm) (entry 6). Using commercially available silica gel-supported thiol (entries 7 and 8), decreased reactivity was observed in DMF at 80 °C (entry 6), but reactivity could be restored at higher temperature (90° C, 97% conversion, 92% yield). However, because this material was prepared via a grafting route, a direct comparison is not feasible.

Although only a few hetereogeneous catalysts have been reported to promote the Suzuki−Miyaura reaction with chloroarenes,[13b,34] we observed complete reaction at temperatures as low as 80−100 °C (Table 2, entry 5 and Table 3, entries

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Table 3. Substrate Scope for the Suzuki−Miyaura Coupling[a]

entry	substrate	solvent	conv. (yield)
1	4-chlorobenzene	DMF	(67)[b]
2	4-chloroacetophenone	H_2O	99 (96)[b]
3	3-bromopyridine	DMF/H_2O	99 (98)
4	4-bromotoluene	DMF/H_2O	(82)[b]
5	4-bromoanisole	H_2O	99 (96)[b]
6	4-bromobenzaldehyde	H_2O	99 (97)[b]

[a] Reactions performed at 90 °C for 15 h with 1% catalyst, and at 100 °C for 24 h with 2% catalyst for chloroarenes. [b] Isolated yields.

Table 4. Reusability of the Catalyst in the Suzuki−Miyaura Reaction of 4-Bromoacetophenone with Phenylboronic Acid

entry	catalyst	solvent	conditions	conv. (yield) (%)
1	SBA-15-SH·Pd	DMF/H_2O	8 h/80 °C	99 (98)
2	1st recycle	DMF/H_2O	8 h/80 °C	99 (97)
3	2nd recycle	DMF/H_2O	8 h/80 °C	98 (97)
4	3rd recycle	DMF/H_2O	8 h/80 °C	96 (95)
5	4th recycle	DMF/H_2O	8 h/80 °C	96 (95)
6	SBA-15-SH·Pd	H_2O	5 h/80 °C	99 (98)
7	1st recycle	H_2O	5 h/80 °C	99 (99)
8	2nd recycle	H_2O	5 h/80 °C	99 (97)
9	3rd recycle	H_2O	5 h/80 °C	98 (96)
10	4th recycle	H_2O	5 h/80 °C	96 (92)
11	SiO_2-SH·Pd	H_2O	5 h/80 °C	96 (95)
12	1st recycle	H_2O	5 h/80 °C	84 (82)
13	2nd recycle	H_2O	5 h/80 °C	81 (78)
14	3rd recycle	H_2O	5 h/80 °C	80 (77)

1 and 2). Various substituted bromo- and chloroarenes were also examined as substrates for the Suzuki−Miyaura coupling (Table 3). Heteroaromatic substrates such as 3-bromopyridine and deactivated substrates such as 4-bromoanisole underwent coupling reactions with good to excellent yields (Table 3).

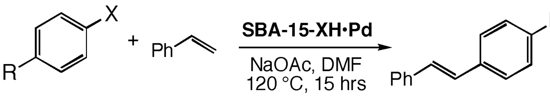
After the completion of the reaction, the catalyst was recovered by filtration using specially made reversible Schlenk frit reactor to prevent materials losses during filtration. After the catalyst was rinsed with dichloromethane or DMF and water under inert atmosphere, a new reaction was performed with fresh solvent and reactants under the same conditions. Interestingly, the silica material showed a noticeable loss in activity after the first reuse, and then the activity remained approximately constant (Table 4). In contrast, the catalyst supported on mesoporous silica could be reused multiple times with virtually no loss of activity, even in water (Table 4).

Mizoroki−Heck Coupling. The Mizoroki−Heck reaction of styrene with bromoacetophenone, bromo, and iodobenzene (eq 2) was also catalyzed by SBA-15-SH·Pd and SBA-15-NH$_2$·Pd (Table 5). Again, the catalyst showed good activity, and Pd leaching was minimal (less than 0.25 ppm, entries 2 and 3). Interestingly, although the amine-functionalized silicate was also an active catalyst, Pd leaching was substantial, 35 ppm, entry 5. This corresponds to almost 10% of the initially added catalyst, illustrating the importance of the thiol-modified surface for retaining Pd.

Heterogeneity Tests. To determine whether the catalyst is actually functioning in a heterogeneous manner, or whether it is merely a reservoir for more active soluble forms of Pd, various heterogeneity tests were performed.

First, the reaction was carried out in the presence of 0.5 ppm of Pd(OAc)$_2$ because traces of Pd have been reported by Leadbeter to have high catalytic activity.[35] After 8 h at 80 °C under otherwise standard conditions, we found less than 5% conversion. In addition, we examined the leaching of Pd at various points in the reaction. With SBA-15-SH-modified materials, we observed the same level of Pd at different points in the reaction, which is inconsistent with a mechanism in which the substrate is removing the Pd from support and the reaction occurring in solution.

Table 5. SBA-15-Modified Pd Catalysts for the Mizoroki−Heck Reaction[a]



(eq. 2)

entry	substrate (R/X)	catalyst (loading)	conv. (yield) (%)	Pd leaching (ppm)
1	H/Br	SBA-15-SH·Pd (1%)	98 (95)	<2[b]
2	COMe/Br	SBA-15-SH·Pd (0.5%)	99 (96)	0.23[c]
3	COMe/Br	reuse (entry 3, 0.5%)	98 (93)	0.27[c]
4	H/I	SBA-15-NH$_2$·Pd (1%)	99 (96)	n.d.
5	H/Br	SBA-15-NH$_2$·Pd (1.5%)	99 (97)	35[b]

[a] Unless otherwise noted, reaction conditions are 120 °C, 1 mmol of halide, 1.5 mmol of olefin, 2 mmol of NaOAc, DMF, 15 h. [b] Determined by atomic absorption. [c] Determined by ICPMS.

A hot-filtration test was also performed,[36] which entails filtering a portion of the solution after the reaction initiates, and before substrate is consumed. After filtration, both portions were heated for a total reaction time of 8 h and the conversion in both samples determined.

We initially employed DMF as solvent and carried out the reaction and filtration in the glovebox to prevent oxidation of the catalyst.[37] After 3 h, the reaction was split at a conversion of 28%. After an additional 5 h, the portion containing the suspended catalyst had proceeded to 97% conversion, while the catalyst free portion reacted only an additional 1%. However, concern over the solubility of K_2CO_3 and PhB(OH)$_2$ in pure DMF and therefore their effective transfer during the filtration led us to repeat this reaction using 4/1 DMF/water, outside the glovebox in a double reactor connected by a frit. Filtration after 1 h (12% conversion) followed by an additional 7 h of reaction gave a final conversion of 97% for the silicate-containing portion, and 17% conversion for the filtered portion. One final split test was performed in which the second flask that received the filtered catalyst had an additional charge of K_2CO_3 and PhB(OH)$_2$. As in the previous case, an 5% additional reaction was observed (Figure 2).

Three-Phase Test. As a final examination of the heterogeneous/homogeneous question, we performed a three-phase test.[38] This test, developed by Rebek and co-workers, is considered to be a definitive test for the presence of catalytically active homogeneous metal species.[38] Corma,[13b,19a] Davies,[39] and others have employed it in a variety of systems. The test consists of covalently immobilizing one of the reaction partners, for example, the aryl halide, and examining its reaction with a soluble reagent (in our case, PhB(OH)$_2$) and the catalyst, supported in a third phase. If the catalyst remains immobilized,

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(35) Arvela, R. K.; Leadbeater, N. E.; Sangi, M. S.; Williams, V. A.; Granados, P.; Singer, R. D. *J. Org. Chem.* **2005**, *70*, 161.

(36) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485.

(37) Although the catalyst is stable in solid form, and few precautions need to be taken at the beginning of the reaction in terms of exclusion of air; the reaction is sensitive to oxygen once it has begun.

(38) (a) Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112. (b) Rebek, J.; Brown, D.; Zimmerman, S. *J. Am. Chem. Soc.* **1975**, *97*, 454.

(39) Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139.

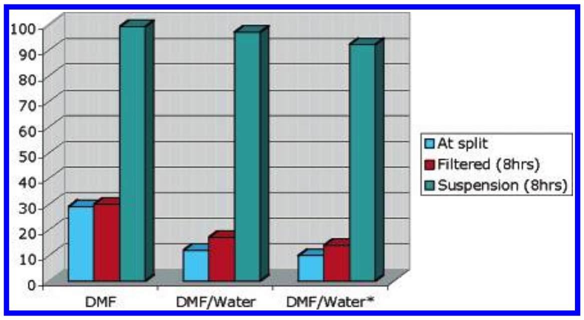
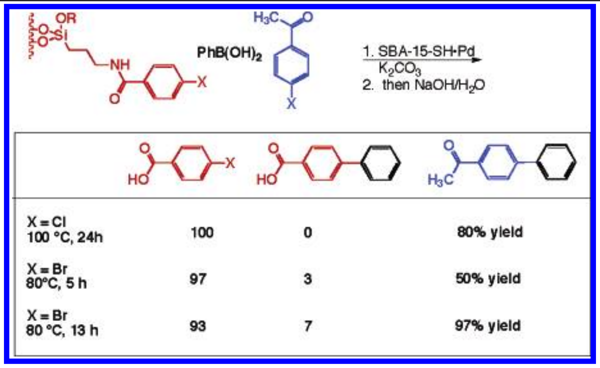


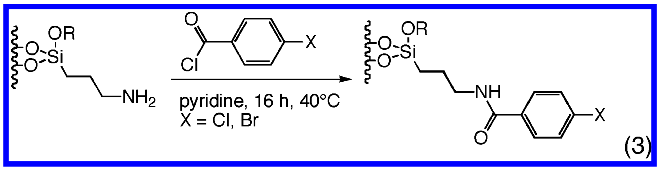
Figure 2. Hot filtration test to determine the presence of catalytically active, homogeneous Pd.

Table 6. Three-Phase Test in the Suzuki−Miyaura Reaction with SBA-15-SH·Pd



X = Cl 100 °C, 24h	100	0	80% yield
X = Br 80°C, 5 h	97	3	50% yield
X = Br 80 °C, 13 h	93	7	97% yield

it will be incapable of accessing the supported aryl halide, but if homogeneous Pd is released, then the supported substrate can be converted into product. In addition, it is critical to add a soluble aryl halide to the reaction to ensure that an active catalyst is present, and also to provide a more correct mimicry of the reaction conditions. For example, Davies et al.[39] showed that a supported aryl iodide was completely inactive in the Pd/C-catalyzed methoxycarbonylation reaction, unless a soluble aryl iodide was added, in which case complete conversion of the immobilized substrate was observed. Thus, we prepared immobilized aryl bromide and chlorides according to the method of Corma et al. (eq 3).[13b]



(3)

The supported aryl chloride and bromide were then subjected to the reaction conditions in the presence of 4-chloroacetophenone and 4-bromoacetophenone, respectively. After reaction, the soluble portion was analyzed by filtration and workup in the usual manner, while the amide was hydrolyzed from the support and isolated as the carboxylic acid (Table 6).

In the case of the immobilized aryl chloride, no reaction was observed on support after 24 h at 100 °C, while the soluble 4-chloroacetophenone substrate reacted in 80% yield. For the supported bromide, unreacted *p*-bromobenzoic acid and *p*-phenylbenzoic acid were observed in a 97:3 ratio after normal reaction conditions (5 h, 80 °C). In addition, 50% of *p*-phenylacetophenone was observed from coupling of the two soluble reagents, indicating the presence of an active catalyst. Even after 13 h, only a 93:7 ratio of *p*-bromobenzoic acid to *p*-phenylbenzoic acid was observed along with 97% conversion of the homogeneous reagents.

These experiments show that, although traces of Pd leach from support and are catalytically active, the large majority of the catalysis is carried out by truly heterogeneous Pd catalyst.

Conclusions

In conclusion, we have shown that thiol-functionalized mesoporous silicates are efficient Pd scavengers and that the resulting Pd encapsulated materials catalyze the Suzuki−Miyaura and Mizoroki−Heck coupling reactions with virtually no leaching of Pd. Several heterogeneity tests were performed on the catalyst under Suzuki−Miyaura conditions and indicate that the majority of the catalysis ($>$95%) occurs on the support via a truly heterogeneous catalyst. Studies are ongoing to determine the structure of the catalyst and the scope of its activity.

Experimental Section

High-resolution TEM (HRTEM) and STM images were obtained with a JEOL 2011 (S)TEM electron microscope operated at 200 kV. X-ray analysis with an EDAX (Genesis) energy-dispersive X-ray system was used to confirm the presence of palladium in samples. N_2 adsorption and desorption isotherms were measured at 77 K. The nitrogen adsorption isotherms were measured using a Micromeritics ASAP 2010 system. The sample was preheated at 100 °C overnight in a vacuum line prior to analysis. The specific surface area and the pore size distribution were calculated using the BET and Barrett−Joyner−Halenda (BJH) methods, respectively.

Preparation of SBA-15-SH or SiO_2-SH by the Grafting Method. Mercaptopropyltrimethoxysilane (1 mL, 5.3 mmol) and pyridine (1 mL, 12.3 mmol) were added dropwise to a suspension of SBA-15[26] or SiO_2 (1 g) in dry toluene (30 mL), under N_2 atmosphere. The resulting mixture was refluxed at 115 °C for 24 h. After cooling, the suspension was filtered and the solid residue was washed with methanol, ether, acetone, and hexane to eliminate unreacted thiol. The resulting solid was dried under vacuum at room temperature, giving a white powder (BET surface area $= 410$ m^2/g for SBA-15-SH; elemental analysis of sulfur $= 2.2$ mmol/g and BET surface area $= 297$ m^2/g for SiO_2-SH and elemental analysis of sulfur $= 1.3$ mmol/g).

Preparation of SBA-15-SH by the Sol−Gel Method. The synthesis of MPTMS-functionalized SBA-15 materials was similar to that of pure-silica SBA-15,[26] except for adding varying amounts of MPTMS. Samples were synthesized by one-step co-condensation of tetraethoxysilane (TEOS) and different proportions of 3-mercaptopropyltrimethoxysilane (MPTMS), which were mixed in advance in the presence of tri-block copolymer Pluronic123 (P123). Varying ratios of TEOS:MPTMS were employed along with 4 g of $(EO)_{20}(PO)_{70}(EO)_{20}$, 120 mL of 2 M HCl, and 30 mL of distilled water. The molar ratio of TEOS:MPTMS follows the formula x moles of TEOS and $(0.041 - x)$ moles of MPTMS, where $x = 0.041$, 0.0385, 0.0376, 0.0368, 0.0347, corresponding to MPTMS concentrations of 0, 6, 8, 10, and 15%, respectively. After aging for 48 h at 80 °C, the solid samples were filtered. Removal of surfactant P123 was conducted by using ethanol extraction at 70 °C for 3 days. The solid sample was filtered and dried at room temperature under vacuum.

Preparation of SBA-15-SH·Pd or SiO_2-SH·Pd. A volume of 50 mL of 0.005 M $Pd(OAc)_2$ in dry THF solution was prepared in a Schlenk flask. To this was added 1 g of SBA-SH or SiO_2-SH, and the mixture was stirred at room temperature for 1 h. The solid catalyst was then filtered and washed with THF and vacuum-dried at room temperature.

Synthesis of Aminopropyl-Modified Silica (SBA-15-NH_2 and SiO_2-15-NH_2). 3-Aminopropyl trimethoxysilane (APTMS) (16 mL, 90 mmol) and pyridine (10 mL, 123 mmol) were added dropwise to a suspension of SiO_2 or SBA-15 (10 g) in dry toluene (30 mL), under N_2 atmosphere. The resulting mixture was refluxed for 24 h. After that time, the suspension was filtered and Soxhlet extracted with dichloromethane for 24 h. The resulting solid was dried under vacuum at room temperature, giving 11.8 g of a white powder.

Scavenging Experiments. Silicates (100 mg) were stirred for 1 h with 10 mL of Pd(II)acetate or chloride solutions of known concentrations. After this time, the solutions were filtered through a PTFE filter, and the Pd concentration left in the supernatant liquids was measured by ICPMS.

Experimental Procedure for Suzuki−Miyaura Coupling. Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), potassium carbonate (2 mmol), hexamethylbenzene (0.5 mmol, as internal standard for GC analysis), and palladium catalyst (1%) were mixed in a sealed tube. 5 mL of solvent (H_2O or DMF or DMF/H_2O mixture (20:1)) was added to this reaction mixture, which was stirred at the desired temperature under inert atmosphere. After completion of the reaction (as determined by GC), the catalyst was filtered and the reaction mixture was poured into water. The aqueous phase was extracted with CH_2Cl_2. After removal of the volatiles in vacuo, the product was purified by column chromatography.

Experimental Procedure for Mizoroki−Heck Coupling. The aryl halide (1 mmol) was mixed with 1.5 mmol of styrene, 2 mmol of sodium acetate, and 0.5−1.5% Pd-silicate catalyst in 5 mL of DMF in a sealed tube. After being purged with nitrogen, the reaction mixture was heated to 120 °C. After completion of the reaction (as determined by GC), the reaction was cooled, the catalyst removed by filtration, and the catalyst washed with CH_2Cl_2. The inorganic salts were removed by extraction with water and CH_2Cl_2. After drying and removal of the volatiles from the organic layer, the product was purified by column chromatography on silica gel.

Three-Phase Tests. Following the procedure of Corma et al.[13b] to prepare silica gel supported substrates, a solution of the corresponding acyl chloride (*p*-chlorobenzoylamide 0.919 g, 5.25 mmol; or *p*-bromobenzoylamide, 1.15 g, 5.25 mmol) was dissolved in dry THF (10 mL) in a round-bottomed flask along with aminopropyl trimethoxysilane-modified silica (1 g, see previously described synthesis) and pyridine (404 μL, 5 mmol), under nitrogen. The resulting suspension was stirred at 40 °C for 12 h, then filtered and washed three times with 20 mL of 5% (v/v) HCl in water, followed by two washes with 20 mL of 0.02 M aqueous K_2CO_3, two washes with distilled water, and two washes with 20 mL of ethanol. The resulting solid was washed with a large excess of dichloromethane and dried in air. In the case of BrPhCONH@SiO_2, 1.178 g was recovered, and for ClPhCONH@SiO_2, 1.13 g was recovered.

A solution of 4-chloroacetophenone or 4-bromoacetophenone (0.25 mmol), phenyl boronic acid (0.37 mmol, 1.5 equiv), and K_2CO_3 (0.5 mmol, 2 equiv) in water was stirred in the presence of SBA-SH·Pd catalyst and ClPhCONH@SiO_2 or BrPhCONH@SiO_2 (250 mg) at 100 °C for 24 h in the case of the chloro substrate, or 80 °C for 5 or 13 h in the case of the bromo substrate. After this time, the supernatant was analyzed by GC and the solid was separated by filtration under vacuum while hot, washed with ethanol, and further extracted with dichloromethane.

The solid was then hydrolyzed with 2 M KOH in ethanol/water (1.68 g in 10 mL of EtOH, 5 mL of H_2O) at 90 °C for 3 days. The resulting solution was neutralized with 10% HCl v/v (9.1 mL), extracted with CH_2Cl_2 followed by ethyl acetate, concentrated, and the resulting mixture was analyzed by ^{1}H NMR.

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Supporting Information Available: TEM and STEM images of selected catalysts, nitrogen adsorption isotherms for catalysts, and powder X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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