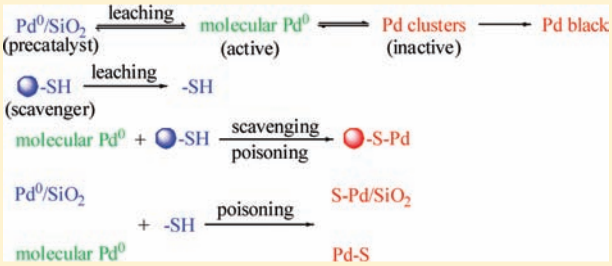
Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

On the Roles of Solid-Bound Ligand Scavengers in the Removal of Palladium Residues and in the Distinction between Homogeneous and Heterogeneous Catalysis

Lin Huang,* Thiam Peng Ang, Zhan Wang, Jozel Tan, Junhui Chen, and Pui Kwan Wong

Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research, 1 Pesek Road, Jurong Island, Singapore 627833, Singapore

Supporting Information



ABSTRACT: We have studied the roles and behavior of typical resin- and silica-bound thiol scavengers in the removal of palladium (Pd) residues and in the determination of the true catalytic species in the Heck coupling of bromobenzene and styrene. The results of Pd scavenging and catalyst poisoning by elemental analysis (EA) and transmission electron microscopy (TEM) indicate that silica-bound thiols have an advantage over resin-bound thiols in residual Pd removal from a Heck reaction solution and that all of these scavengers poison effectively the catalytic species but hardly scavenge Pd clusters, even as small as 1 nm from solution presumably because of the steric barrier. Because of a smaller proportion of soluble Pd clusters, using a molecular Pd precatalyst results in a much higher Pd scavenging efficiency than using a supported Pd particle precatalyst. With the aid of catalyst poisoning by the scavengers, filtration testing and TEM studies further illustrate that Pd clusters are inactive for the Heck reaction over Pd^0/SiO_2, with molecular Pd^0 being solely active. Studies through EA and thermogravimetric analysis suggest that the bound thiols are leached from the scavengers to a different extent at reaction temperatures of 90−135 °C, probably owing to base-catalyzed decomposition or based-promoted dissociation of functional groups from the surfaces, leading to interaction between leached thiols and a solid Pd precatalyst. Meanwhile, the effect of solid-bound thiol binding to soluble Pd on the efficiency of Pd scavenging and the impact of a scavenger on the Pd leaching from supported Pd particles are discussed.

INTRODUCTION

Compared to the understanding of heterogeneous catalysts in gas−solid-phase reactions, which is a well-developed area of science, the understanding of the nature of the true active species using solid precatalysts in liquid−solid-phase reactions remains poor. Sometimes solids act as true catalysts, with the reaction occurring on the solid surfaces, whereas sometimes leached soluble species play a real catalytic role. Indeed, in palladium (Pd)-catalyzed C−C coupling reactions, the latter has proven to be the case with many solid Pd precatalysts. The "homogeneous" nature of catalysis is suggested, although solid Pd precatalysts are used.[1,2]

Thus far, the nature of catalysis for C−C coupling reactions with solid Pd precatalysts remains a fundamental debate as to whether the active species virtually involve soluble molecular Pd species (single type of active center), which are called homogeneous catalysts, or soluble Pd clusters and/or solid Pd particles (multiple types of active centers), which are classified as heterogeneous catalysts.[3,4] Generally, a mixed catalyst system consisting of soluble molecular Pd species, soluble Pd clusters, and solid Pd particles may possibly contain both homogeneous and heterogeneous active species. If homogeneous active species dominate catalysis despite a tiny contribution of heterogeneous active species, then the nature of catalysis is referred to as homogeneous. This is also the reasoning for the heterogeneous nature of catalysis. We understand that soluble molecular Pd was predominantly active in most cases where the nature of catalysis was suggested to be homogeneous,[1,5−21] while soluble Pd clusters or solid Pd particles were much more active in some few cases where the nature of catalysis was hypothesized to be heterogeneous.[22−31] Several methods can be used to assess the nature of the true catalyst with solid Pd precatalysts such as immobilized Pd−ligand complexes and supported Pd particles in C−C coupling chemistry, including poisoning by mercury(0) (Hg^0), catalyst poisoning, kinetic testing, surface technique, filtration (or split) testing, and three-phase testing.[1,2,4] In the investigation of the catalysis heterogeneity of solid Pd precatalysts, control experiments are devised to probe the potential leaching of active or inactive Pd from solid Pd precatalysts. Scavenging of leached soluble Pd is an important way of poisoning "homogeneous" active species in a mixed catalyst system, which permits us to shed light on whether the contribution of "homogeneous" active species to catalysis of the whole system is eliminated. It is known that the ppb or even ppt levels of soluble Pd are sufficient to catalyze C−C coupling reactions in

Received: April 27, 2010
Published: February 21, 2011

some cases.[32−34] As such, efficiently scavenging or poisoning leached soluble Pd so as to extinguish its catalysis will help reveal whether the reaction proceeds uniquely on immobilized Pd—ligand complexes or on supported Pd particles.

A diverse variety of scavengers have been developed to treat the reaction solution for the purpose of reducing the Pd contamination to acceptable levels toward the product after catalytic reaction, which include trimercaptotriazine (TMT), polystyrene-bound TMT, MP-TMT, polystyrene-bound ethylenediamine, activated carbon, glass bead sponges, smopex, polymer-bound ligands, and silica-bound ligands. Their application is summarized in a comprehensive review by Garrett and Prasad[35] and published in recent articles.[36−38] Among these scavengers, organic or inorganic solid-bound ligand materials were demonstrated to be promising for the efficient removal Pd of from organic and aqueous solutions. For instance, polystyrene-bound TMT was used to purify aqueous and organic solutions containing Pd^{II}.[39] After a solution containing 60 ppm of Pd with 3.8 equiv of TMT per Pd^{II} was stirred at or below pH 2.2 at room temperature for 1 day, over 99.8% Pd could be removed. Smopex fibers that contain grafted functional groups were used to treat mixture solutions from coupling reactions.[40] After treatment of a liquor solution containing 395 ppm of Pd with about 1.1% Smopex-110 at room temperature overnight, the Pd concentration was reduced to 3 ppm. After treatment of a methanol solution containing 23 ppm of Pd with a mixture of Smopex-101 and -105 at room temperature for 30 min, the Pd concentration was reduced to less than 1 ppm. Silica-bound thiols (SH-silica) were examined for their Pd-scavenging ability in aqueous and organic solutions[26,41,42] and applied in the residual Pd removal from reaction products.[36,38] At initial $PdCl_2$ concentrations of 100−850 ppm in water, more than 99.5% Pd could be removed at room temperature within 1 h using 100 mg of SH-SBA-15 (2.2 mmol/g of S) or SH-SiO_2 (1.3 mmol/g of S). At an initial palladium acetate concentration of 1000 ppm in tetrahydrofuran (THF), more than 99% Pd could be eliminated by 4 equiv of SH-SiO_2 at room temperature within 1 h. At an initial residual Pd concentration of 2100 ppm in a liquor solution of the Suzuki coupling product, scavenging could give a product with less than 2 ppm of residual Pd using a method of gravity elution through a SH-SiO_2 (1 g, 1.0 mmol/g of S) cartridge.

Inspired by the exciting performance of the solid-bound ligand or insoluble scavengers in the reduction of Pd contamination, people began to take an interest in exploiting such kinds of solid materials as selective poisons for soluble Pd catalysts to discriminate between homogeneous and heterogeneous catalysis.[7,8,27,28,43−54] By the addition of an insoluble poison to a reaction system with a solid Pd precatalyst, soluble active Pd species leached from the solid Pd precatalyst could be pulled out of the solution and deactivated by scavenging, so that the catalytic activity of the system could be attributed to solid Pd active sites. The resulting activity would be interpreted as evidence for the identity of catalysis, provided the insoluble poison interacted rarely with the solid Pd active sites. If it were zero, the same as that without the insoluble poison, and lower than that without the insoluble poison, then the identity of catalysis would be suggested to be "homogeneous", heterogeneous, and "homogeneous"/heterogeneous, respectively. Several groups positively used poly(4-vinylpyridine) (PVPy) as a Pd^{II} trap to test the catalysis heterogeneity over solid Pd precatalysts,[7,27,43−47,49−53] in that pyridines are known to bind strongly to Pd^{II}.[43,55] Typically, Yu, Sommer, Weck, Richardson, and Jones et al. applied this poisoning to show precatalyst decomposition to form soluble Pd catalytic species from an array of SiO_2- and polymer-tethered Pd pincer complexes in the Heck coupling of iodobenzene (PhI) and *n*-butyl acrylate.[43−45] They suggested that leached soluble Pd from polymer-entrapped palladium acetate is responsible for the Heck reaction based on deactivation of the catalyst system in the presence of PVPy.[49] Ji et al. reported that PVPy is able to quench the Heck coupling of PhI and *n*-butyl acrylate either over palladium acetate or over SiO_2-supported Pd particles via complexation with soluble Pd^{II} of palladium acetate or soluble Pd^{II} of PhPdI issued by the oxidative addition of PhI to the supported Pd particles.[47] They thus concluded that the activity over Pd^0/SiO_2 is from leached soluble Pd. Probably because of the restriction of PVPy in application and its limited ability to poison soluble Pd^{II}, some groups chose to adopt polymer- and silica-bound thiols as effective poisons to deactivate soluble Pd catalysts derived from solid Pd precatalysts.[8,27,28,48,49] Immobilized thiols were demonstrated to have a strong ability to scavenge molecular Pd^0 and Pd^{II}[8,26,41,42,49] and reported to reduce the Pd level in solution more effectively than immobilized amines.[26,42] Cessation of a reaction upon the addition of such a poison is expectedly rapid and efficient if soluble Pd leached from a solid Pd precatalyst is solely active. Richardson and Jones studied solution-phase catalysis in connection with Pd leaching from poly(urea)-entrapped Pd and SBA-15-tethered Pd during the Heck coupling of PhI and *n*-butyl acrylate and the Suzuki coupling of bromoacetophenone and phenylboronic acid.[8,49] They found that QuadraPure TU (TU), SH-SBA-15, and SH-SiO_2 can be successfully used as effective poisons of the leached soluble Pd to shutdown catalysis of the systems studied, which can rule out catalysis by the immobilized Pd. They also pointed out that SH-SBA-15 and SH-SiO_2 are a better class of poisons for soluble Pd than TU in effectiveness and versatility.[8] Jana et al. investigated Heck and Sonogashira couplings over a silicate MCM-41-immobilized Pd^0 precatalyst.[28] They noted that Pd^0/MCM-41 is impressively active for the activation of chlorobenzene (PhCl) so that PhCl conversions can reach 15−45 and 30% in Heck and Sonogashira couplings of PhCl at 100 °C, respectively. In the meantime, they examined the catalysis heterogeneity in Heck and Sonogashira couplings over Pd^0/MCM-41. They did not observe any influence of the addition of SH-MCM-41 or SH-SiO_2 as a poison on the catalytic results as well as did not detect any Pd leaching in the liquid phase from Pd^0/MCM-41 during the reactions. Their findings suggested that no Pd leaching occurs in the reactions over Pd^0/MCM-41 and that Pd^0/MCM-41 acts as a true heterogeneous catalyst in the reactions.

This article reports more complete studies on the roles and behavior of resin- and silica-bound thiol scavengers in the Heck coupling of bromobenzene (PhBr) and styrene over conventionally prepared Pd^0/SiO_2 in order to elucidate the nature of the true catalytic species, as well as in the removal of soluble Pd in different forms. Inexpensive amorphous silica is one of the most commonly used supports for preparing heterogeneous metal catalysts. It possesses the advantage of good stability in mechanics and chemistry. Pd particles supported on SiO_2, which are most representative, are prepared from Pd^{II}/SiO_2 using a prereduction method.[15,56−58] Insoluble resin- and silica-bound thiols are viewed as excellent scavengers and/or poisons for soluble Pd.[8,26−28,34,36,38,41,42,48,49,59−61] Their use should preferentially suppress catalysis due to soluble Pd without affecting possible active sites of the vast majority of the Pd particles that are supported on an internal surface of SiO_2 if they are stable under reaction conditions, because such insoluble resins and silica should not access the pores of SiO_2.[43,45,47] At the same time

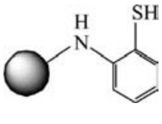


Figure 1. Structure of MPA.

that we present the results of Pd scavenging and the performance of such scavengers in the poisoning of soluble Pd catalysts, we provide the analytical data of both the liquid and solid phases in reaction systems by means of elemental analysis (EA) and thermogravimetric analysis (TGA) for clarifying the leachings of Pd and ligands and the indirect interaction between solid-bound ligands and Pd^0/SiO_2. The previous studies have merely shown the ability of similar scavengers to remove Pd from solution and their performance in the poisoning of soluble Pd leached from solid Pd precatalysts with almost no concerns about leaching of the ligands and its influence on the catalytic results and Pd leaching.[61] Also, we tentatively assess the abilities of such scavengers to scavenge both molecular Pd and Pd clusters present in solution in terms of analytical data, filtration testing, and transmission electron microscopy (TEM) evidence. We aimed to gain an understanding of the respective contributions of molecular Pd and Pd clusters to catalysis in solution. Through a study of selective poisoning in a soluble Pd mixture, we further suggest which kind of Pd species is the true catalyst in soluble Pd. The previous studies have only considered poisoning of the soluble Pd species active for C−C coupling reactions without differentiation between molecular Pd and Pd clusters. There has been a lack of understanding on the scavenging of Pd clusters from solution with solid-bound ligand scavengers previously.

EXPERIMENTAL SECTION

Silica gel [SiO_2; 366 m^2/g Brunauer−Emmett−Teller (BET) surface area], MCM-41-type mesostructured silica (MCM-41; 750 m^2/g BET surface area), QuadraPure MPA (MPA; 1.5 mmol S/g), 3-mercaptopropyl-functionalized silica gel (SH-SiO_2; 1.2 mmol S/g), palladium acetylacetonate [$Pd(acac)_2$; 99%], palladium acetate (98%), PhBr (99%), styrene (>99%), anhydrous Na_2CO_3 (≥99.5%), anhydrous NaOAc (≥99%), (3-mercaptopropyl)trimethoxysilane [$HS(CH_2)_3Si(OCH_3)_3$; 95%], and anhydrous *N*,*N*-dimethylacetamide (DMA; 99.8%) were purchased from Sigma-Aldrich. MPA belongs to a QuadraPure-functionalized microporous resin series with excellent scavenging properties, especially for Pd, at different pH values and in the presence of competing ligands and substrates.[59,60] Its structure is depicted in Figure 1. The gases Ar and N_2 used had a purity of 99.999%.

The conventional solid precatalyst Pd^0/SiO_2 (1.1% of Pd loading) was prepared as described previously.[15] SH-MCM-41 was achieved by reacting MCM-41 (2.0 g) with $HS(CH_2)_3Si(OCH_3)_3$ (1.5 g) in toluene (70 mL) at reflux temperature under Ar for 19 h. The resulting solid was then filtered off, washed with toluene, methanol, acetone, hexanes, and acetone again, and dried overnight at 50 °C under vacuum. Loadings of 1.2−1.9 mmol of S/g were found by EA. SH-MCM-41 thus obtained, MPA, and SH-SiO_2 purchased were used without further treatment. For the preparation of $HS(CH_2)_3Si(OCH_3)_3$-complexed Pd^{II}, $Pd(acac)_2$ (0.004 g) and $HS(CH_2)_3Si(OCH_3)_3$ (S:Pd = 3:1 atomic ratio) were stirred in DMA (4 mL) under Ar at room temperature for 16 h. The resultant brown $Pd^{II}/HS(CH_2)_3Si(OCH_3)_3$ solution was directly used as soluble thiol-complexed Pd^{II} in Heck reactions. For the preparation of MPA- or SH-MCM-41-tethered Pd^{II}, MPA or SH-MCM-41 (0.5 g) was stirred with a DMA solution of $Pd(acac)_2$ (0.014 g) under Ar at room temperature for 16 h. The resultant red Pd^{II}/MPA or brown Pd^{II}/SH-MCM-41 was filtered off and washed with DMA and CH_2Cl_2, followed by drying at room temperature under vacuum. DMA was dried and stored over dehydrated 5 Å molecular sieves before use.

Catalytic testing in the Heck coupling of PhBr and styrene was performed as follows. PhBr (10 mmol), styrene (15 mmol), Na_2CO_3 (5 mmol) or NaOAc (10 mmol), Pd^0/SiO_2 (0.08 g, 0.078 mol % of Pd relative to PhBr) or $Pd(acac)_2$ (10 ppm of Pd), and DMA (10 mL) were introduced to a three-necked flask under Ar. After the mixture had been stirred at room temperature for 10 min under Ar, the flask was placed in a preheated oil bath with vigorous stirring (500 rpm). The reaction solution was sampled at reaction temperature and atmosphere using 0.45 μm Whatman syringe filters through a septum. In a scavenging or poisoning experiment, the scavenger (0.08 g) was added to a solution or reaction system at reaction temperature and atmosphere. The atomic ratios of S on the scavengers to Pd in $Pd(acac)_2$ were 101:1 for MPA, 82:1 for SH-SiO_2, and 126:1 for SH-MCM-41, respectively. The atomic ratios of S on the scavengers to Pd in Pd^0/SiO_2 were 16:1 for MPA, 13:1 for SH-SiO_2, and 20:1 for SH-MCM-41, respectively. The S/Pd atomic ratios used in this work were, in principle, high enough to scavenge removable Pd in solution.[8,26,39,41,49] In a filtration test, the reaction solution was drawn off through a 0.45 μm Whatman syringe filter at reaction temperature and atmosphere and transferred into another flask having Na_2CO_3 (5 mmol) or NaOAc (10 mmol) under Ar. The reaction was quickly initiated with the filtrate under equivalent conditions. The blank test with DMA alone showed that there was neither detectable Pd in the filtrate nor catalytic activity over the filtrate. All samples collected for analysis and characterization were stored under Ar prior to use. Exceptions to the reaction conditions described above are noted where necessary.

The reactants and products in the samples were analyzed by gas chromatography on a Perkin-Elmer Clarus 500 gas chromatograph. After the Heck reaction or scavenging experiment had been stopped, the solid mixture was carefully filtered off and washed with DMA, deionized water, and CH_2Cl_2, followed by drying at 110 °C under vacuum. For the Pd/SiO_2 + scavenger mixture, the mass ratio of Pd/SiO_2 to scavenger was approximately regarded as 1:1. The mixture following drying was subjected to analysis without separation. Our comparative experiments verified that this mass ratio remained substantially unchanged after reaction, filtration, washing, and drying. The Pd contents in solution and solid samples were determined by the inductively coupled plasma (ICP) technique on a Varian Vista-MPX CCD simultaneous ICP-OES spectrograph (Supporting Information). The experimentation for determination of the Pd contents by the ICP technique was described previously.[15] The S and N contents in the solid samples were determined using a EURO 3000 C,H,N,S elemental analyzer. The amounts and thermal stability of the functional groups on the scavengers were estimated by TGA in N_2 or air using a TGA Q500 analyzer. The microscopic images of Pd clusters produced in solution were observed by TEM on a JEOL TecnaiG^2 microscope. A small amount of solution containing possibly Pd clusters was dipped onto a carbon-coated copper grip followed by autoevaporation of the solvent at room temperature. Pd clusters were identified by energy-dispersive X-ray analysis (EDX). The Pd cluster size distributions were determined by counting the sizes of 100−200 clusters on several images taken from different places. The evolution of $Pd(acac)_2$ in solution during thermal treatment or a Heck reaction was followed by ultraviolet and visible (UV−vis) absorption spectroscopy on a Shimadzu UV-2550 spectrophotometer.

RESULTS AND DISCUSSION

Pd Scavenging and Catalyst Poisoning in DMA-Dissolved $Pd(acac)_2$ Systems. The complexation efficiency of a solid scavenger with soluble metal or a soluble metal compound determines the extent of removal of soluble metal or a soluble metal compound, relying on several factors including the functional group—metal center reactivity, metal valence, metal environment, medium, and temperature. SH-silica was reported to exhibit excellent abilities to scavenge soluble Pd^{II} in water and in THF[26,41,42] and to remove soluble Pd from a liquor solution of Suzuki coupling products.[36,38] TU was shown to efficiently capture Pd residues from a solution of Heck coupling products.[37] Nonetheless, the scavenging capacities of these scavengers for soluble Pd^{II} and Pd^0 in commonly used solvents in C—C coupling reactions and their behavior during scavenging are not clear. We began with measurement of the Pd scavenging capacities of MPA, SH-SiO$_2$, and SH-MCM-41 for Pd(acac)$_2$ systems in DMA. In order to make scavenging conditions closer to those of our Heck reactions in the presence of solid Pd precatalysts, an initial Pd concentration of 10 ppm and a scavenging temperature of 135 °C were chosen, mainly considering the practical levels of Pd leaching into solution.

In Table 1 are compared the efficiencies of Pd(acac)$_2$ scavenging with SH-SiO$_2$ from some commonly used organic solvents. A total of 60 min of scavenging at room temperature discriminated between favorable and disadvantageous organic solvents for complexation of SH-SiO$_2$ with Pd(acac)$_2$ in terms of solid color change and solution ICP analysis. That the scavenger color deepens with an increase in the adsorbed Pd(acac)$_2$ amount matches the solution ICP analytical results. The property of the organic solvent does have a marked impact on the efficiency of metal compound scavenging. The relative efficiency of Pd(acac)$_2$ scavenging from these solvents was shown in the order of hexanes = ethanol > DMA > toluene > THF. Only 51.8% Pd(acac)$_2$ can be removed from DMA after 60 min of scavenging with SH-SiO$_2$ at room temperature. The ability of scavengers like SH-SiO$_2$ to complex a Pd compound dissolved in different solvents may rely on their steric accessibility and the competing interaction of solvents with the Pd compound. The observed difference in the Pd(acac)$_2$ scavenging efficiency may be associated with the integrated levels of these surrounding solvent molecules in steric protection of Pd(acac)$_2$ and interaction with Pd(acac)$_2$.

Table 1. Scavenging of Pd(acac)$_2$ (10 ppm of Pd) in Different Organic Solvents with SH-SiO$_2$ at Room Temperature[a]

	after treatment		
solvent	solid color[b]	[Pd] (ppm)	Pd removed (%)
hexanes	brown	0.23	97.7
THF	yellow	7.96	20.4
toluene	yellow	6.60	34.0
ethanol	brown	0.23	97.7
DMA	deep yellow	4.82	51.8

[a] Solutions (10 mL) of Pd(acac)$_2$ (10 ppm of Pd) stirred with 0.08 g of SH-SiO$_2$ at room temperature under Ar for 60 min. [b] SH-SiO$_2$ was white in color.

In a further experiment of Pd compound scavenging from DMA, a DMA (10 mL) solution of Pd compound (10 ppm of Pd) was previously stirred at 135 °C under Ar for 10 min and 0.08 g of scavenger was added to it. The resulting system was further stirred at 135 °C under Ar. Table 2 presents the EA results during the scavenging processes of Pd compounds in DMA by the scavengers. In the case with Pd(acac)$_2$, 10 min of heating did not result in any change in solution before the addition of a scavenger. Even after 30 min of heating, the solution was kept nearly colorless and the UV—vis absorption band of Pd(acac)$_2$ in DMA at 327.5 nm[62] remained substantially unchanged in intensity, as shown in Figure 2, which accounts for the fact that Pd(acac)$_2$ is stable in DMA at 135 °C. The addition of the scavengers led to removal of only 61—82% Pd from solution, and 2—4 ppm of residual Pd still remained. The relative ability of the scavengers to scavenge Pd(acac)$_2$ in DMA was observed in the order of SH-MCM-41 > SH-SiO$_2$ > MPA. From an electronic standpoint, $HS(C_6H_4)$ (*o*-NH) present on MPA has a stronger ability to complex a metal center than silica-bound $HS(CH_2)_3Si$. The observed converse ability to scavenge Pd(acac)$_2$ is presumably due to the steric effect

Table 2. Scavenging of Pd Compounds (10 ppm of Pd) in DMA with Solid-Bound Thiols at 135 °C[a]

		after treatment			[S]/scavenger (%)	
Pd compound	scavenger	time (min)	[Pd] (ppm)	Pd removed (%)	before treatment	after treatment
Pd(acac)$_2$	MPA	10	3.73	62.7		
		30	3.89	61.1	4.0	4.0
		60	3.32	66.8	4.0	4.0
	SH-SiO$_2$	10	2.95	70.7		
		30	2.57	74.3	3.6	3.6
		60	2.99	70.1		
	SH-SiO$_2$[b]	10	7.22	27.8		
		60	4.82	51.8		
	SH-MCM-41	10	2.17	78.3		
		30	3.27	67.3	6.2	6.2
		60	1.81	81.9		
palladium acetate	MPA	10	9.13	8.7		
		30	7.74	22.6		
		60	6.64	33.6	4.0	4.0
	SH-SiO$_2$	30	6.19	38.1		
		240	3.75	62.5	3.6	3.6

[a] A total of 0.08 g of scavenger was added to a DMA (10 mL) solution of Pd compound (10 ppm of Pd), which had been preheated at 135 °C under Ar for 10 min, and the resulting system was further stirred at 135 °C under Ar. [b] Reaction and scavenging conducted at room temperature.

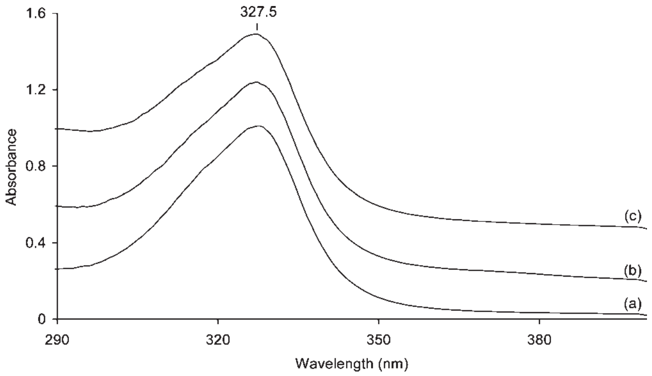


Figure 2. UV−vis spectra of $Pd(acac)_2$ in DMA (10 ppm of Pd) after treatment under Ar at (a) room temperature, (b) 135 °C for 10 min, and (c) 135 °C for 30 min.

between bound ligand and $Pd(acac)_2$. $HS(C_6H_4)(o\text{-}NH)$ is more bulky than $HS(CH_2)_3Si$, and the Pd^{II} center is surrounded by the acetylacetonyl groups, making a steric barrier. This situation renders MPA less accessible to the Pd^{II} center than SH-silica. An extended treatment exceeding 10 min seemed to improve the Pd removal efficiency rather slowly. Compared to the scavenging results at room temperature, the high Pd removal efficiency with $SH\text{-}SiO_2$ at 135 °C signifies the importance of the scavenging temperature for complexation of the bound thiols with soluble Pd. In the case with palladium acetate, much lower scavenging efficiencies were observed, although they increased with the scavenging time. At 135 °C, only 33.6% palladium acetate was removed after 1 h of scavenging with MPA, and only 62.5% palladium acetate was scavenged after 4 h of scavenging with $SH\text{-}SiO_2$. Apparently, the ability of these solid-bound thiols to scavenge $Pd(acac)_2$ or palladium acetate from a DMA solution is not as high as expected from other cases reported.[26,41,42] Concurrent with the Pd analysis in solution, the S analysis in the solid phase indicated that the bound thiols were not leached out of the scavengers during scavenging treatments at 135 °C.

In an experiment of Pd scavenging and catalyst poisoning, a Heck reaction of PhBr and styrene was run in the presence of Na_2CO_3 over $Pd(acac)_2$ (10 ppm of Pd) in DMA (10 mL) at 135 °C under Ar to 30 min and a scavenger (0.08 g) was added to the reaction system. The resulting system was further stirred at 135 °C under Ar. It is known that $Pd(acac)_2$ is readily reduced to form soluble Pd^0 species including molecular Pd^0 (more likely monomeric Pd^0) and Pd clusters as well as black Pd precipitates under the reaction conditions.[15,63,64] After the reaction system had been heated at 135 °C for 5 min, the nearly colorless reaction solution turned yellow, the 327.5 nm band in the UV−vis spectrum due to $Pd(acac)_2$ disappeared in favor of the appearance of bands of the Heck reaction products, as shown in Figure 3. It is difficult to track the evolution of the 327.5 nm band because it overlaps much with those of the Heck reaction products. We thus managed to retard the catalytic reaction by disusing the base. In the absence of the base, only trace amounts of the Heck reaction products were formed and their UV−vis bands observed at 311.3 and 325.5 nm were much less intense (Figure 3b−d). It is evident that, once $Pd(acac)_2$ was heated with the reactants at 135 °C, the 327.5 nm band disappeared. Meanwhile, careful examination of the UV−vis spectra verifies that no absorption bands were discerned in the region from 330 nm onward. Combined with our recent TEM study,[15] these UV−vis observations may be indicative of the prompt reduction of $Pd(acac)_2$ in the reaction media at 135 °C to form Pd nanoclusters of below 10 nm size.[65,66] It has been reported that the resonance band of Pd nanotubes of 8 nm size falls at about 225 nm,[65,67] while the resonance bands of 25 and 50 nm Pd nanotubes are located at around 330 and 390 nm, respectively.[65] Unfortunately, the 225 nm band position is covered by the very intense spectrum of DMA in our case. After 30 min of the Heck reaction over $Pd(acac)_2$, $Pd(acac)_2$ has been transformed into molecular Pd^0, Pd clusters, and Pd black, with Pd clusters remaining as the minor part.[15] Of all Pd species derived from Pd compounds such as palladium acetate and $Pd(acac)_2$, only molecular Pd^0 is deemed to be the active species for C−C coupling reactions.[5,6,8,15,68]

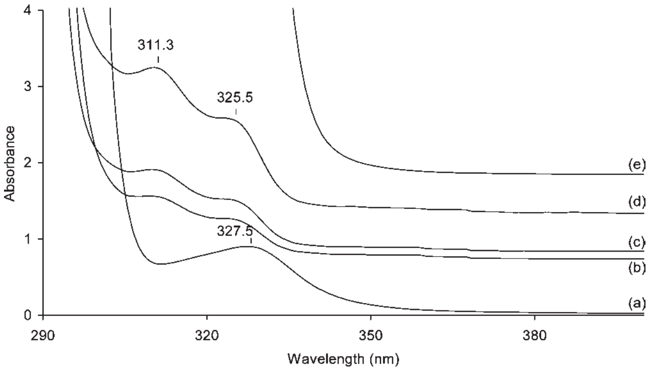


Figure 3. UV−vis spectra of $Pd(acac)_2$-containing reaction solutions (10 ppm of Pd) after treatment under Ar at (a) room temperature in the absence of the base, (b) 135 °C in the absence of the base for 2 min, (c) 135 °C in the absence of the base for 5 min, (d) 135 °C in the absence of the base for 10 min, and (e) 135 °C in the presence of Na_2CO_3 for 5 min.

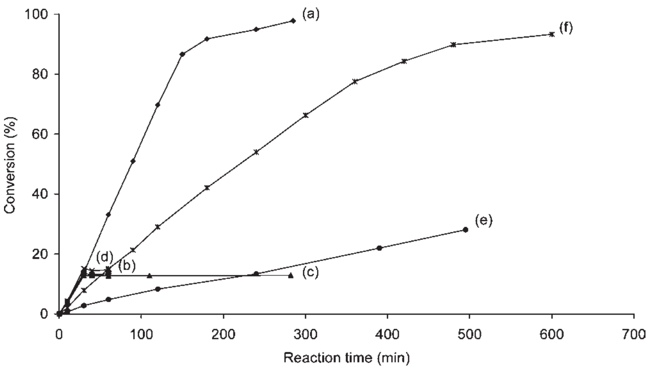


Figure 4. Heck coupling profiles of PhBr and styrene in the presence of Na_2CO_3 at 135 °C over (a) $Pd(acac)_2$ (10 ppm of Pd), (b) $Pd(acac)_2$ (10 ppm of Pd) for 30 min followed by the addition of MPA, (c) $Pd(acac)_2$ (10 ppm of Pd) for 30 min followed by the addition of $SH\text{-}SiO_2$, (d) $Pd(acac)_2$ (10 ppm of Pd) for 30 min followed by the addition of SH-MCM-41, (e) $Pd(acac)_2$ (0.1 ppm of Pd), and (f) $Pd(acac)_2$ (0.5 ppm of Pd).

Figure 4 and Table 3 show the poisoning effect of the scavengers on the Heck reaction over $Pd(acac)_2$ and the related EA data during the poisoning processes, respectively. The $Pd(acac)_2$ system, which showed a high catalytic activity for the Heck reaction (Figure 4a), was completely deactivated once any of the scavengers was added (Figure 4b−d). There was no more growth in PhBr conversion within a few hours in the presence of any of the scavengers. This demonstrates that molecular Pd^0 as the active species derived from $Pd(acac)_2$ is efficiently poisoned

Table 3. Scavenging of Pd with Solid-Bound Thiols during the Heck Coupling of PhBr and Styrene over $Pd(acac)_2$ (10 ppm of Pd) in DMA in the Presence of Na_2CO_3 at 135 °C[a]

	before addition		after addition			decrement (%)	
scavenger	[Pd] (ppm)	[S]/scavenger (%)	time (min)	[Pd] (ppm)	[S]/scavenger (%)	Pd	S
MPA	7.16	4.0	10	0.80	3.5	88.8	12.5
			30	0.50	2.6	93.0	35.0
MPA[b]	8.14	4.0	30	0.54	4.0	93.4	0
SH-SiO_2	8.37	3.6	10	1.60	3.4	80.9	5.6
			30	1.41	3.2	83.2	11.1
SH-SiO_2[b]	9.34	3.6	30	1.40	3.6	85.0	0
SH-MCM-41	6.65	6.2	10	0.64	5.9	90.4	4.8
			30	0.25	5.7	96.2	8.1
SH-MCM-41[b]	8.32	6.2	30	0.36	6.2	95.7	0

[a] A total of 0.08 g of scavenger was added to the reaction system when the Heck reaction proceeded to 30 min at 135 °C under Ar, and the resulting system was further stirred at 135 °C under Ar. [b] Reaction and scavenging conducted in the absence of Na_2CO_3; a total 0.08 g of scavenger was added to the reaction system when the Heck reaction proceeded to 10 min at 135 °C under Ar.

by any of the scavengers. In the scavenging and poisoning processes, more than 80% Pd was removed and only less than 1.6 ppm of residual Pd was retained after 10 min of treatment using these scavengers. After 30 min of treatment, the Pd removal efficiencies reached 93 and 96% with MPA and SH-MCM-41, respectively. TEM—EDX observations confirmed the presence of large amounts of Pd clusters in the reaction solution after the catalyst poisoning (Supporting Information), supporting the hypothesis of the inactivity of Pd clusters.[6] Before and after Pd scavenging, the densities of the Pd clusters looked likely comparable in view of TEM images, and the Pd cluster size distribution remained basically unchanged. It thus does not seem that Pd scavenging has an effect on the removal of Pd clusters from solution. Under reaction conditions, $Pd(acac)_2$ is reduced with the disappearance of acetylacetonyls. Without the steric barrier, the observed ability of MPA to scavenge soluble Pd is no longer worse than that of SH-silica (Table 3). Meanwhile, a noticeable amount of S was lost from all of the scavengers according to EA, which was an indication that significant thiol leaching occurred during the scavenging treatments at 135 °C. The thiol leaching from MPA was serious.

To determine whether the base used in the Heck reactions is responsible for leaching of the functional groups, we conducted a series of complementary Pd scavenging experiments under equivalent conditions. In a typical experiment, a DMA (10 mL) solution of $Pd(acac)_2$ (10 ppm of Pd), PhBr, and styrene was previously stirred in the absence of the base at 135 °C under Ar for 10 min and a scavenger (0.08 g) was added to the system. The resulting system was further stirred at 135 °C under Ar. As is the case where the base was used, 5 min of heating led to the appearance of a yellow color in solution before Pd scavenging, which could indicate the occurrence of easy reduction of $Pd(acac)_2$ in solution, as shown by UV—vis in Figure 3. After 30 min of Pd scavenging, all of the scavengers displayed Pd scavenging efficiencies as good as when the base was used (Table 3). Concurrently, EA indicated that no leaching of the functional groups on any of the scavengers occurred during Pd scavenging (Table 3), demonstrating the role played by the base in leaching of the functional groups.

The EA data can gain support from the TGA study. In Figure 5 are compared the TGA profiles in N_2 at a heating rate of 10 °C/min of MPA before and after Pd scavenging in the Heck reaction over $Pd(acac)_2$ (10 ppm of Pd) in DMA at 135 °C under Ar. The decomposing temperatures of the functional groups and polymer backbone of fresh MPA ranged roughly from 160 to 300 °C and from 350 to 450 °C, respectively, in accordance with the thermal decomposition studies reported for quaternary ammonium-functionalized poly(methylstyrene-*co*-styrene) resins by TGA, EA, and Volhard analysis.[69] After 30 min of Pd scavenging in the absence of the base, the weight loss of recovered MPA at 160—300 °C remained essentially unchanged. In contrast, the related weight loss depleted obviously after Pd scavenging in the presence of Na_2CO_3: The depletion was significant after 10 min and serious after 30 min. This shows that the functional groups are easily decomposed from MPA in the presence of Na_2CO_3 under reaction conditions. What is more, we noticed that decomposition was accelerated by Pd because the Pd dependence of the functional group loss in the presence of Na_2CO_3 was observed by TGA (Supporting Information). The TGA results of SH-SiO_2 and SH-MCM-41 before and after Pd scavenging indicate that the attached thiols are thermally much more stable and that only low thiol leaching occurs (Supporting Information).

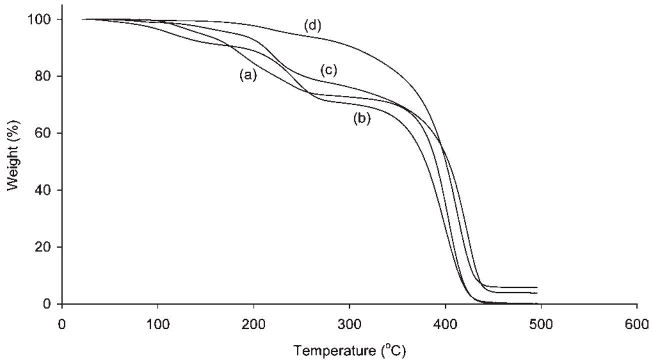


Figure 5. TGA profiles in N_2 at a heating rate of 10 °C/min of (a) fresh MPA, (b) recovered MPA after 30 min of Pd scavenging in the Heck coupling of PhBr and styrene over $Pd(acac)_2$ (10 ppm of Pd) in the absence of the base at 135 °C, (c) recovered MPA after 10 min of Pd scavenging in the Heck coupling of PhBr and styrene over $Pd(acac)_2$ (10 ppm of Pd) in the presence of Na_2CO_3 at 135 °C, and (d) recovered MPA after 30 min of Pd scavenging in the Heck coupling of PhBr and styrene over $Pd(acac)_2$ (10 ppm of Pd) in the presence of Na_2CO_3 at 135 °C.

Combination of the catalytic and analytical data clearly reflects that, despite the fact that the catalytic activity of the system is suppressed by any of the scavengers, small amounts of Pd species still remain and cannot be removed from solution under the conditions used here. These remaining soluble Pd species are by no means active. Note that even less than 0.1 ppm of the active Pd species is sufficient to bring about a notable increase in PhBr conversion within 30 min, as shown in Figure 4e. The inactive Pd species relate most probably to Pd clusters and/or thiol-complexed Pd (Pd—S).[6,8,15] Pd—S may be formed via complexation of thiols leached from the scavengers with soluble Pd. Afterall, the molar numbers of leached thiols far surpass that of the remaining Pd in DMA. In the cases of 5.6% S leached from SH-SiO_2 and 4.8% S leached from SH-MCM-41, the S/Pd atomic ratios attain 24 and 63, respectively. A total of 4.8—35.0% thiol leaching represents a considerably high S/Pd atomic ratio in solution and thus a strong complexation probability between leached thiols and the remaining soluble Pd. On the other hand, solid-bound Pd—S resulting through Pd scavenging also may leach part of Pd—S into solution.

Besides the influence of solvent on $Pd(acac)_2$ scavenging, the comparative analytical results show that Pd scavenging can be remarkably improved under these reaction conditions compared to the situation of $Pd(acac)_2$ alone in DMA. In a given solvent, Pd^{II} is sterically protected by acetylacetonyls in the form of $Pd(acac)_2$. Solid-bound thiols bind to such Pd^{II} with difficulty. For palladium acetate, the steric effect is more pronounced. Although the acetyl group is less bulky than the acetylacetonyl group, the steric barrier of Pd^{II} seems greater in palladium acetate than in $Pd(acac)_2$ because of the structure of $[Pd(OAc)_2]_3$ aggregates.[70] The trimeric structure of palladium acetate has been demonstrated to persist in solution.[71,72] As a consequence, the observed Pd^{II} scavenging capacity of the scavengers is not high in $Pd(acac)_2$ and is even lower in palladium acetate. It would follow that the low $Pd(acac)_2$ scavenging efficiency with the scavengers in DMA is mainly due to the steric barrier by acetylacetonyls as well as to the influence of DMA. Note that $Pd(acac)_2$ is relatively stable in DMA at 135 °C and is hardly reduced by DMA alone. With such a steric barrier, the geometric factor of bound ligand seems more important than its electronic factor in complexation with Pd^{II}. The bulky ligand $HS(C_6H_4)(o\text{-}NH)$ enables MPA to be less efficient than SH-silica in $Pd(acac)_2$ scavenging. The Heck reaction media, especially the alkene, likely play a key role in the reduction of $Pd(acac)_2$ in DMA.[9,73] Under the reaction conditions, $Pd(acac)_2$ is virtually destroyed and transformed to soluble Pd and Pd black. With the steric barrier by acetylacetonyls having been eliminated, binding of a scavenger to Pd proceeds smoothly. The electronic factor of bound ligand seems to become salient in complexation with Pd^0. MPA hence becomes no less efficient than SH-silica in Pd scavenging, despite the presence of heavier thiol leaching, which leads to the production of much more Pd—S in solution (Table 3).

It is important to point out that the base used in Heck reactions has a critical impact on leaching of the functional groups from the scavengers. Our EA and TGA results clearly justify that the use of Na_2CO_3 is the crucial origin of the functional group leaching from the scavengers under the reaction conditions. Under such a basic condition, some relevant chemistry may favorably occur with the scavengers. QuadraPure scavengers like MPA are functionalized polystyrene-based resins.[74] The only issue in the chemical stability of such resins is known to involve decomposition of the functional groups and depolymerization catalyzed by bases.[69,75−79] Previous work has demonstrated that thermal decomposition of the functional groups in the resins begins from 160 °C[69] and that the use of bases promotes degradation of the polymer resins.[75−79] The fact that leaching of the functional groups from MPA takes place only with the presence of Na_2CO_3 at 135 °C leads us to assume that Na_2CO_3 catalyzes decomposition of the functional groups from MPA while a Heck reaction proceeds. On the basis of the fact that Pd speeds up decomposition of the functional groups with the presence of the base but does not act without the presence of the base, we would regard Pd only as a promoter rather than a catalyst. The effect of Pd on thermal decomposition of the polymers is not yet known, although some metal elements such as iron, nickel, and copper have been reported to promote the degradation of polymer materials.[80−82] On the other hand, the base-promoted dissociation of functional groups from the silica surface may be proposed for thiol leaching from SH-SiO_2 or SH-MCM-41, although mercaptopropyl groups on silica are much more stable than functional groups on QuadraPure materials.[83,84] With a weakly acidic organic solvent like DMA, dissociation may be assumed to occur with the aid of a base like Na_2CO_3 via cleavage of the Si—O—Si bonds in the functional groups, similar to hydrolysis of the Si—O—Si bonds on the MCM-41 surface.[85,86] It is unclear whether these leaching results are entirely applicable to other bases and solvents used in C—C coupling reactions.

Generally, the factors causing leaching of the functional groups from solid scavengers during a C—C coupling reaction include the basicity of the solution (pK_b and concentration of a base in a solvent), solvent, and temperature. Leaching of the functional groups appears to be sensitive to the basicity of the reaction solution because it occurs readily even in the presence of weak inorganic bases like NaOAc (as shown later). Na_2CO_3 and NaOAc are typical inorganic bases used in C—C coupling reactions. Their use in the present Heck reaction only gives rise to a low basicity to the reaction solution because of their tiny solubility in DMA (Supporting Information). An important role of reaction solvents in leaching of the functional groups from solid scavengers is to dissolve solid bases more or less. To prevent cleavage of the Si—O—Si bonds, solvents used should be neutral. The reaction temperature matters much to decomposition and dissociation of the functional groups. To prevent leaching of the functional groups, scavenging or poisoning experiments should be performed at temperatures as low as possible.

Pd Scavenging and Catalyst Poisoning over Pd^0/SiO_2. On the basis of the results of Pd scavenging and catalyst poisoning obtained in the above $Pd(acac)_2$ systems, we intended to focus our studies on the situation of conventionally prepared Pd^0/SiO_2 as the precatalyst in the Heck coupling of PhBr and styrene. Let us take an overall look at the roles and behavior of those solid-bound thiols in soluble Pd scavenging and catalyst poisoning with Pd^0/SiO_2 and the impact of their behavior on the solid Pd precatalyst under the reaction conditions.

In a first array of scavenging and poisoning experiments, Heck reactions were carried out in the presence of Na_2CO_3 over Pd^0/SiO_2 at 135 °C under Ar for 60 min before a scavenger was added. The resulting systems were further stirred at 135 °C under Ar. Our recent work has demonstrated that under Heck reaction conditions, soluble Pd contains a higher fraction of Pd clusters over Pd^0/SiO_2 than over $Pd(acac)_2$ and that the fraction of Pd clusters in solution increases slowly as a Heck reaction proceeds over Pd^0/SiO_2.[15] Figure 6 and Tables 4 and 5 show the poisoning effect of the scavengers on catalysis, the soluble Pd scavenging, and the mutual impact between scavenger and the supported Pd particles in leaching in the whole process. After the addition of any of the scavengers, a low activity that the Pd^0/SiO_2 system had for the Heck reaction (Figure 6a) was rapidly quenched (Figure 6b−d). There was almost no increase any longer in PhBr conversion within at least 1 h in the presence of any of the scavengers. This unambiguity indicates that all of the possible catalytic species in the system responsible for the Heck reaction have been effectively poisoned by any of the scavengers. In the scavenging and poisoning processes, it was surprisingly found that the soluble Pd was hardly removed in contrast to the case of the $Pd(acac)_2$-derived catalyst system, with the Pd removal efficiency being rather low (Table 4). At 10 min, the Pd removal efficiency with MPA attained 29.5%, which was obviously superior to that with SH-silica (<23%). However, it diminished with the scavenging time. At 30 and 60 min, it became much lower than that of SH-silica. At 60 min, only 13.0−36.0% soluble Pd was removed with these scavengers. In order to avoid the influence of Pd^0/SiO_2 on Pd scavenging, we conducted a Pd scavenging experiment in a reaction filtrate with $SH\text{-}SiO_2$. After 1 h of scavenging under identical conditions, the Pd removal efficiency was only 37.7%, similar to that when Pd^0/SiO_2 was present (Table 4). This result is of significance for evaluation of the Pd scavenging efficiency from solution after C−C coupling reactions over solid Pd precatalysts. It was also surprisingly observed that the supported Pd was rapidly lost from the solid phase (Pd^0/SiO_2 + scavenger) compared with the individual case of Pd^0/SiO_2 (Table 5). As for the bound functional groups, their amounts were noted to progressively come off the solid phase as the scavenging and poisoning proceeded (Table 5). In the presence of an effective scavenger, Pd leached out of supported Pd may be present as soluble Pd clusters, soluble Pd complexes, and scavenged Pd and Pd black, which are all catalytically inactive. In the presence of supported Pd, functional groups leached out of a scavenger may exist in the forms of soluble free ligands, soluble Pd complexes, and ligands adsorbed on supported Pd. In contrast to the individual case of Pd^0/SiO_2, where the Pd loss from Pd^0/SiO_2 was only 5.5 and 24.5% after 2 and 10 h of Heck reaction, the addition of any of the scavengers, especially MPA, resulted in considerable Pd loss from Pd^0/SiO_2 within a short time. The loss of functional groups from the solid phase increased with the reaction time to different extents. It was serious in the case with MPA, where some 55% of functional groups vanished from the solid phase after 1 h of Pd scavenging.

Consistent with the EA data, the TGA study of recovered Pd^0/SiO_2 + scavenger after Pd scavenging in the Heck reaction also indicated that thiol loss from the solid phase rose with an increase in the scavenging time (Supporting Information). This was obviously reflected in the TGA of recovered Pd^0/SiO_2 + MPA.

It is necessary to point out that in the case where no Pd loss or low Pd loss from the solid phase (Pd^0/SiO_2 + scavenger) takes place, leached Pd from Pd^0/SiO_2 may be scavenged by a scavenger. Likewise, in the case of no thiol loss or low thiol loss from the solid phase, the possibility that leached thiols from a scavenger may be adsorbed onto SiO_2-supported Pd particles cannot be ruled out. In the presence of any of the scavengers, the increased Pd concentration in solution after 30 min may be directly associated with the increased Pd and thiol losses from the solid phase. Such soluble Pd consists of Pd clusters and Pd−S

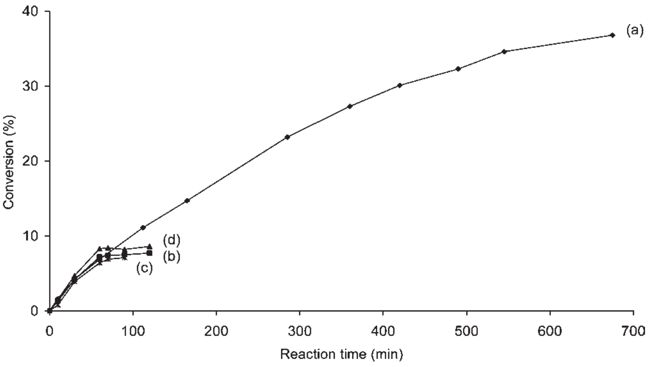


Figure 6. Heck coupling profiles of PhBr and styrene in the presence of Na_2CO_3 at 135 °C over (a) Pd^0/SiO_2, (b) Pd^0/SiO_2 for 60 min followed by the addition of MPA, (c) Pd^0/SiO_2 for 60 min followed by the addition of $SH\text{-}SiO_2$, and (d) Pd^0/SiO_2 for 60 min followed by the addition of SH-MCM-41.

Table 5. EA of Solid Precatalysts and Scavengers before and after the Addition of Scavengers following 1 h of Heck Coupling of PhBr and Styrene over Pd^0/SiO_2 in the Presence of Na_2CO_3 at 135 °C

	before addition (%)			after addition (%)				decrement (%)		
scavenger	[Pd]	[S]	[N]	time	[Pd]	[S]	[N]	Pd	S	N
	1.1			2 h	1.0			9.1		
				10 h	0.83			24.5		
MPA	1.1	4.0	2.0	10 min	0.24	2.0	1.0	56.4	0	0
				30 min		1.3	0.7		35.0	35.0
				60 min	0.22	0.9	0.46	60.0	55.0	54.0
				4 h		0.36	0.23		82.0	77.0
$SH\text{-}SiO_2$	1.1	3.6		10 min	0.5	1.8		9.1	0	
				30 min	0.48	1.7		12.7	5.6	
SH-MCM-41	1.1	6.2		10 min	0.5	3.1		9.1	0	
				60 min	0.47	2.9		14.5	6.5	

Table 4. Leached Pd Concentrations in Solution before and after the Addition of Scavengers following 1 h of Heck Coupling of PhBr and Styrene over Pd^0/SiO_2 in the Presence of Na_2CO_3 at 135 °C

		after addition [Pd] (ppm)			Pd removed (%)		
scavenger	before addition [Pd] (ppm)	10 min	30 min	60 min	10 min	30 min	60 min
MPA	3.08	2.17	2.27	2.68	29.5	26.3	13.0
$SH\text{-}SiO_2$	3.28	2.64	0.88	2.10	19.5	73.2	36.0
$SH\text{-}SiO_2$[a]	3.79	2.04	1.94	2.36	46.2	48.8	37.7
SH-MCM-41	3.36	2.59	0.70	2.21	22.9	79.2	34.2

[a] $SH\text{-}SiO_2$ was added to the reaction filtrate following 1 h of the Heck reaction under identical conditions.

without molecular Pd because the system is no longer catalytically active although the soluble Pd concentration is not low. Most of the Pd lost from the solid phase is deemed to transform to Pd black. Black metal precipitates were obviously observed in the reaction mixture in the case with MPA as the scavenger.

In a second array of scavenging and poisoning experiments, Heck reactions were run in the presence of NaOAc over Pd^0/SiO_2 + scavenger or Pd^{II}/scavenger at 135 °C under Ar. Except that the amount of either Pd^0/SiO_2 or scavenger was increased to 0.15 g, the other reaction conditions remained identical. As the Pd leaching proceeds together with a C−C coupling reaction on a halide, the continuous catalyst poisoning by a scavenger depends basically on the speed of Pd leaching, the speed of the oxidative addition of the halide to leached active Pd in the catalytic reaction, and the molar ratio of the functional groups on the scavenger to Pd on the support. Catalytic and analytical data during the Heck reaction can be used to elucidate the ability of such a scavenger to poison the catalytic species and the mechanism of Pd leaching under the influence of the scavenger. Although the basicity of NaOAc in the reaction solution is lower than that of Na_2CO_3 (Supporting Information), the activities for the Heck coupling of PhBr and styrene in the presence of these two bases are similar.[15,21] The use of NaOAc instead of Na_2CO_3 would not significantly alter the behavior of Pd^0/SiO_2 and the scavengers (as shown below). Figures 7 and 8 and Table 6 present the poisoning effect of the scavengers on catalysis, the concentrations of soluble Pd in the poisoning processes, and the mutual impact between the scavenger and the supported Pd particles in leaching. Throughout 5.5 h of the Heck reaction over Pd^0/SiO_2 + MPA, no catalytic activity was detected in the system (Figure 7b). Concurrently, it was unexpected that the concentration of soluble Pd ascended rapidly with the reaction time (Figure 8b) and that the amounts of Pd and functional groups in the solid phase declined obviously with the reaction time (Table 6). The decreasing trend of Pd in the solid phase was consistent with the increasing trend of soluble Pd, indicating a transformation of the supported Pd to soluble Pd. The results show that MPA has not only a strong ability to poison the catalytic species for the Heck reaction over Pd^0/SiO_2 but also a strong promoting effect on Pd leaching. According to the Pd balance in the system, part of the leached Pd is supposed to give rise to Pd black. Black metal precipitates were indeed observed in the reaction mixture. In this case, Pd leaching into solution behaved unusually and Pd scavenging operated unlikely. As a result of the high loss of functional groups from the solid phase, the inactive soluble Pd is supposed to contain mostly Pd−S. To gain an understanding on the mechanism of Pd leaching occurring in the presence of MPA, we inspected the behavior of Pd^{II}/MPA under equivalent conditions. While there was no catalytic activity over Pd^{II}/MPA for an identical reaction time, tremendous Pd leaching into solution

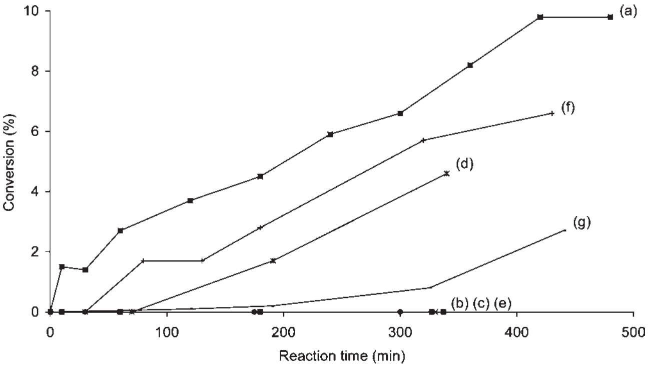


Figure 7. Heck coupling profiles of PhBr and styrene in the presence of NaOAc at 135 °C over (a) Pd^0/SiO_2, (b) Pd^0/SiO_2 + MPA, (c) Pd^{II}/MPA, (d) Pd^0/SiO_2 + SH-MCM-41, (e) Pd^{II}/SH-MCM-41, (f) Pd^0/SiO_2 + SH-SiO_2 (S:Pd = 7:1 atomic ratio) and (g) Pd^0/SiO_2 + SH-SiO_2 (S:Pd = 53:1 atomic ratio).

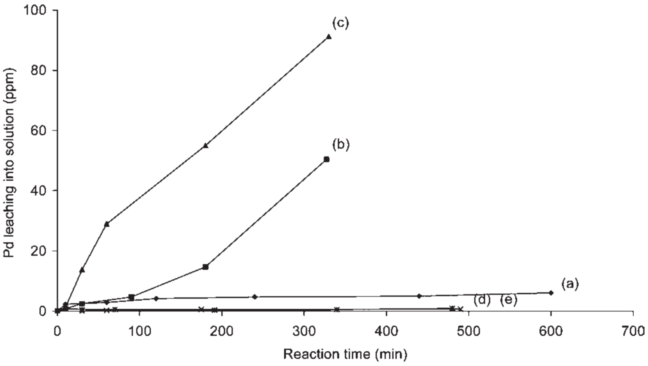
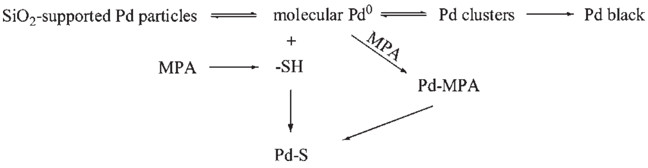


Figure 8. Pd leaching into solution profiles during the Heck coupling of PhBr and styrene in the presence of NaOAc at 135 °C over (a) Pd^0/SiO_2, (b) Pd^0/SiO_2 + MPA, (c) Pd^{II}/MPA, (d) Pd^0/SiO_2 + SH-MCM-41, and (e) Pd^{II}/SH-MCM-41.

Table 6. EA of Solid Precatalysts and Scavengers before and after the Heck Coupling of PhBr and Styrene over Pd^0/SiO_2 in the Presence of NaOAc at 135 °C

	before reaction (%)			after reaction (%)				decrement (%)		
precatalyst + scavenger	[Pd]	[S]	[N]	time (h)	[Pd]	[S]	[N]	Pd	S	N
Pd^0/SiO_2	1.1			10	0.90			18.2		
Pd^0/SiO_2 + MPA	0.55	2.1	1.0	1.5	0.46	2.1	0.93	16.4	0	7.0
				3		1.6	0.77		23.8	23.0
				5.5	0.22	0.75	0.39	60.0	64.3	61.0
Pd^{II}/MPA	0.78	4.1	1.9	1.5	0.41	2.8	1.4	47.4	31.7	26.3
				5.5	0	2.3	1.2	100	43.9	36.8
Pd^0/SiO_2 + SH-MCM-41	0.55	3.1		1	0.49	2.9		10.9	6.5	
				8	0.50	2.7		9.1	12.9	
Pd^{II}/SH-MCM-41	0.84	6.2		1		5.8			6.5	
				8	0.82	5.5		2.4	11.3	

Scheme 1. Suggested Outline of Pd Leaching from Pd^0/SiO_2 in the Presence of MPA during the Heck Reaction



and high Pd and thiol losses from Pd^{II}/MPA occurred simultaneously. This clearly illustrates that thiols and Pd−S on MPA are unstable and are readily leached into solution under the reaction conditions and that no free molecular Pd^0 is present in solution. On the basis of the similarity of Pd^0/SiO_2 + MPA and Pd^{II}/MPA in Pd and thiol leachings, we suggest that excess Pd leaching into solution from Pd^0/SiO_2 + MPA proceeds primarily via Pd scavenging to form Pd−MPA followed by dissociation of Pd−S or via combination of leached thiols with leached Pd to produce Pd−S in solution, as shown in Scheme 1.

By contrast, negligible Pd leaching into solution and low Pd and thiol losses from the solid phase occurred throughout the Heck reaction over Pd^0/SiO_2 + SH-MCM-41. No catalytic activity was discerned in the system until 70 min of reaction, after which the kinetic pattern with a low catalytic activity (Figure 7d) resembled that over Pd^0/SiO_2. In accordance with the EA data, TGA significantly showed no notable change in functional group loss from recovered Pd^0/SiO_2 + SH-MCM-41 after 8 h of Pd scavenging, as seen in Figure 9a. These results may imply that, because of low thiol leaching into solution, some amounts of free molecular Pd^0 are dissociated from Pd clusters through equilibrium shift, which can react with PhBr to enter the catalytic cycle and thus can catalyze the Heck reaction even in the presence of the solid-bound thiols. Similar Heck reaction profiles were observed over Pd^0/SiO_2 + SH-SiO_2 (Figure 7f,g). The catalytic activity fell with an increase in the S/Pd ratio but still appeared during an extended reaction at a S/Pd atomic ratio as high as 53:1. Perhaps, either the S/Pd ratios used in this work may not be sufficient for the solid-bound thiols to completely poison the active Pd leached from Pd^0/SiO_2 in a long reaction or poisoning of the active Pd of such a catalytic system by the solid-bound thiols may be limited. Unless important amounts of thiols are leached into solution from solid scavengers like in the case with Pd^0/SiO_2 + MPA, solid-bound thiols seem markedly less effective than soluble thiols for complexing or poisoning of the active Pd species. Meanwhile, Pd^{II}/SH-MCM-41 had no activity throughout the Heck reaction. It displayed negligible Pd leaching into solution, negligible Pd loss, and low thiol loss. The leached Pd into solution occupies only 0.6% of the Pd loading on Pd^{II}/SH-MCM-41 (Supporting Information). Similar to the case with Pd^0/SiO_2 + SH-MCM-41, TGA indicated a small decrease in functional group loss from recovered Pd^{II}/SH-MCM-41 after 8 h of Pd scavenging (Figure 9b), which is also consistent with the EA data. These observations clearly indicate that MCM-41-bound Pd−S is stable and that no free molecular Pd^0 is produced in solution from Pd^{II}/SH-MCM-41 under the reaction conditions. The results account for the fact that the use of SH-MCM-41 as an excellent catalyst poison also depresses Pd leaching into solution from Pd^0/SiO_2. Therefore, we infer that, in the presence of SH-MCM-41, Pd leaching into solution from Pd^0/SiO_2 goes mainly via aggregation of a minor part of molecular Pd^0 to Pd clusters because of scavenging of a major part of molecular Pd^0 by SH-MCM-41, as shown in Scheme 2. Owing to the good stability of SH-MCM-41 and MCM-41-bound Pd−S, the soluble inactive Pd is assumed to contain mostly Pd clusters in the case with Pd^0/SiO_2 + SH-MCM-41 (Supporting Information). In addition, the observed low Pd decrease in the solid phase was not necessarily an implication of low Pd loss from Pd^0/SiO_2. More Pd may be leached out of Pd^0/SiO_2, and most of the leached Pd may be scavenged onto SH-MCM-41. The degree of Pd loss from Pd^0/SiO_2 or the amount of Pd scavenged by SH-MCM-41 in Pd^0/SiO_2 + SH-MCM-41 during the Heck reaction remains unclear.

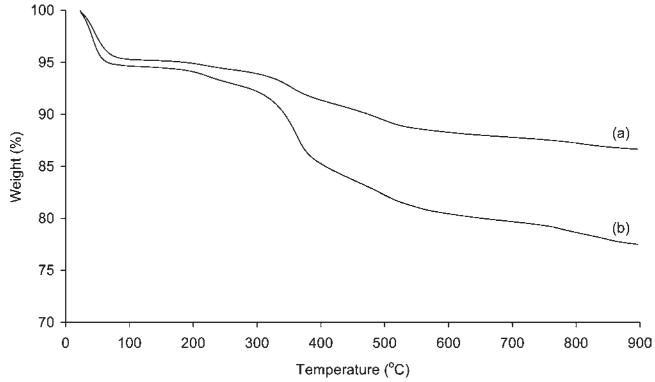
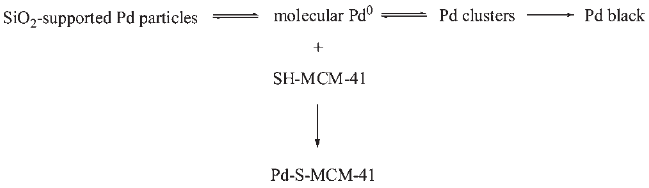


Figure 9. TGA profiles in N_2 at a heating rate of 10 °C/min of recovered solid samples after 8 h of Pd scavenging in the Heck coupling of PhBr and styrene in the presence of NaOAc at 135 °C over (a) Pd^0/SiO_2 + SH-MCM-41 and (b) Pd^{II}/SH-MCM-41.

Scheme 2. Suggested Outline of Pd Scavenging by SH-MCM-41 during the Heck Reaction over Pd^0/SiO_2



In order to gain more insight into the poisoning effect of leached thiols on the catalysis, we ran further Heck reactions with $Pd^{II}/HS(CH_2)_3Si(OCH_3)_3$, Pd^0/SiO_2 + $HS(CH_2)_3Si(OCH_3)_3$, $Pd(acac)_2$ (118 ppm of Pd) + SH-SiO_2, and $Pd(acac)_2$ (118 ppm of Pd) + $HS(CH_2)_3Si(OCH_3)_3$ under equivalent conditions. We compared the poisoning effects of $HS(CH_2)_3Si(OCH_3)_3$ and SH-SiO_2 on catalysis, as shown in Figure 10. The $Pd^{II}/HS(CH_2)_3Si(OCH_3)_3$ system with a S:Pd = 3:1 atomic ratio was absolutely inactive throughout 13 h of the Heck reaction (Figure 10a). This clearly indicates that Pd−S dissociates by no means to produce free molecular Pd^0 in solution even at a S/Pd atomic ratio as low as 3:1. This result further demonstrates the catalytic inactivity of Pd^{II}/MPA and Pd^{II}/SH-MCM-41 regardless of the concomitant high thiol leaching into solution. The thiol groups on MPA have a stronger ability to complex molecular Pd^0 than $HS(CH_2)_3Si(OCH_3)_3$, so that the resulting Pd−S is more stable even if leached from MPA. As expected, $HS(CH_2)_3Si(OCH_3)_3$ was much more effective than SH-silica in the poisoning of catalysis over Pd^0/SiO_2. Close Heck reaction profiles were obtained over Pd^0/SiO_2 + $HS(CH_2)_3Si(OCH_3)_3$ with a S:Pd = 3:1 atomic ratio and over Pd^0/SiO_2 + SH-SiO_2 with a S:Pd = 53:1 atomic ratio. Following

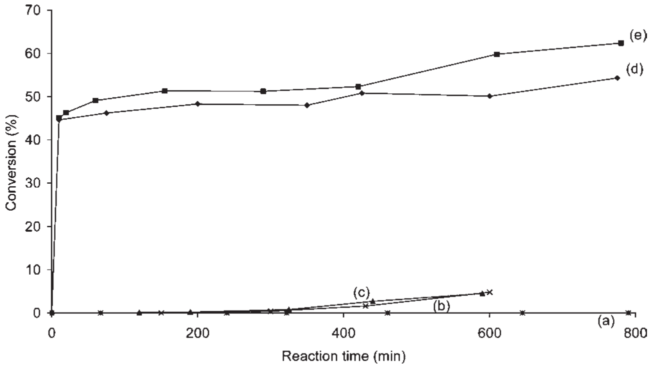


Figure 10. Heck coupling profiles of PhBr and styrene in the presence of NaOAc at 135 °C over (a) $Pd^{II}/HS(CH_2)_3Si(OCH_3)_3$ (118 ppm of Pd; S:Pd = 3:1 atomic ratio), (b) $Pd^0/SiO_2 + HS(CH_2)_3Si(OCH_3)_3$ (S:Pd = 3:1 atomic ratio), (c) Pd^0/SiO_2 + SH-SiO_2 (S:Pd = 53:1 atomic ratio), (d) $Pd(acac)_2$ (118 ppm of Pd) for 10 min followed by the addition of $HS(CH_2)_3Si(OCH_3)_3$ (S:Pd = 3:1 atomic ratio), and (e) $Pd(acac)_2$ (118 ppm of Pd) for 10 min followed by the addition of SH-SiO_2 (S:Pd = 53:1 atomic ratio).

10 min of the Heck reaction over $Pd(acac)_2$ (118 ppm of Pd), the addition of either $HS(CH_2)_3Si(OCH_3)_3$ (S:Pd = 3:1 atomic ratio) or SH-SiO_2 (S:Pd = 53:1 atomic ratio) resulted in immediate cessation of the speedy reaction with the appearance of a new reaction profile in which the conversion rose very slowly with the reaction time. The tiny catalytic activity is undoubtedly attributed to trace amounts of free molecular Pd^0 dissociated from soluble Pd clusters that are derived from $Pd(acac)_2$. Despite the fact that the active Pd derived from $Pd(acac)_2$ could be thoroughly complexed (poisoned) by either of these two scavengers, some amounts of soluble Pd clusters seemed to always be present in the system and give rise to free molecular Pd^0 by the equilibrium shift. These data further illustrate that, during the Heck reaction over Pd^0/SiO_2 + scavenger, the amount of leached thiols from MPA is considerable, whereas that from SH-silica is small because the deactivation extents of the Pd^0/SiO_2 system are quite different in the presence of the two kinds of scavengers.

During Pd scavenging with MPA over Pd^0/SiO_2, the EA data in Tables 5 and 6 indicate that the important loss of Pd is accompanied by the loss of no thiols from the solid phase at initial scavenging stages. The observed loss of no thiols in Pd^0/SiO_2 + MPA does not necessarily imply leaching of no thiols from MPA. It may be possible that the bound thiols are leached out of MPA and subsequently held on SiO_2-supported Pd particles. How much of thiols is leached from MPA to transfer onto SiO_2-supported Pd particles is unknown from our experiments. However, we have found that thiol leaching from MPA occurs significantly at the initial scavenging stage in the absence of Pd^0/SiO_2, as seen in Tables 3 and 6. The difference in thiol loss from the solid phase in the presence and absence of Pd^0/SiO_2 seems to support the assumption that the bound thiols are leached out of MPA and held on SiO_2-supported Pd particles in Pd^0/SiO_2 + MPA under the reaction conditions. Furthermore, we have noticed that thiol loss from Pd^0/SiO_2 + MPA increases obviously as Pd scavenging proceeds, as shown in Tables 5 and 6 and in the Supporting Information. This likely implies that the bound thiols are continuously leached from MPA as long as MPA is present in the system. We thus speculate that the thiols leached from MPA transfer preferentially onto SiO_2-supported Pd particles until their maximal adsorption at the first stage, after which they started to enter into the solution because of no more adsorption sites were available on Pd^0/SiO_2. Besides, the high thiol loss from Pd^0/SiO_2 + MPA detected by EA and TGA is consistent with the lasting deactivation of this system in the Heck reaction due to the efficient production of Pd—S in solution. In a similar manner, the bound thiols may be leached out of SH-MCM-41 and subsequently held on SiO_2-supported Pd particles. By virtue of the EA data in Tables 3, 5, and 6 and the TGA results (Supporting Information), we believe that thiol leaching from SH-MCM-41 takes place once the Heck reaction proceeds over Pd^0/SiO_2 + SH-MCM-41. On the other hand, the low thiol loss from Pd^0/SiO_2 + SH-MCM-41 determined by EA and TGA is consistent with the observed activity of this system in the Heck reaction owing to the favorable formation of free molecular Pd in the presence of a limited amount of leached thiols in solution.

In a third array of scavenging and poisoning experiments, Heck reactions were conducted in the presence of Na_2CO_3 over Pd^0/SiO_2 at 90 °C under Ar to 60 min before a scavenger was added. The resulting systems were further stirred at 90 °C under Ar. The purpose of lowering the reaction temperature was to reduce Pd leaching into solution, on the one hand,[86] and to avoid leaching of the functional groups, on the other hand. Similar to what has been observed at 135 °C, the addition of the scavengers led to cessation of the reaction over Pd^0/SiO_2 (Supporting Information). This shows that the scavengers are effective at poisoning all of the possible catalytic active species at 90 °C as well. In the meantime, removal of soluble Pd was still inefficient under the reaction conditions at 90 °C (Supporting Information). The amount of soluble Pd even increased upon the addition of a scavenger. The addition of the scavengers still resulted in an important Pd loss from Pd^0/SiO_2 at 90 °C (Supporting Information). Most of the Pd lost from the solid phase is believed to convert to Pd black. Black metal precipitates were obviously observed in the reaction mixture in the case with MPA as the scavenger. According to EA, large amounts of functional groups came off Pd^0/SiO_2 + MPA after 60 min of Pd scavenging (Supporting Information). Consistent with the EA data, TGA showed a serious fall in the functional group loss from recovered Pd^0/SiO_2 + MPA after 60 min of Pd scavenging (Supporting Information). The results account for the fact that leaching of the functional groups from MPA still takes place during Pd scavenging at 90 °C. Although silica-bound thiols are much more stable than thiols on MPA, it is difficult to judge from the results whether silica-bound thiols remain without leaching during Pd scavenging at 90 °C, as discussed previously herein.

The results of these three arrays of experiments generally indicate that the catalytic species with Pd^0/SiO_2 can be effectively poisoned by the scavengers similar to the case with the $Pd(acac)_2$ system, but the leached soluble Pd can hardly be removed by the scavengers. The effectiveness of catalyst poisoning by our scavengers in the Heck coupling of PhBr and styrene over Pd^0/SiO_2 is in good agreement with previous reports on Pd catalyst deactivation by similar solid-bound thiol scavengers in C—C coupling reactions.[8,27,28,48,49] There is no doubt that these resin- and silica-bound thiols are excellent poisons or scavengers of the leached Pd active for Heck reactions. However, poisoning of the active Pd does not mean effective Pd scavenging from solution. To date, only a limited number of studies have been reported concerning Pd removal from a post-C—C-coupling solution using solid ligand scavengers.[36−38,40,88,89] Not in all of the cases, scavenging could reduce residual Pd to acceptable levels. The Pd scavenging efficiency of a bound ligand scavenger was found to vary from reaction to reaction.[36] Using an identical scavenger SH-SiO_2, Pd scavenging efficiencies of 99.95 and 79.70% were achieved after Suzuki and Heck reactions, respectively. The scavenging results of post-Heck-coupling products were systematically unsatisfactory regardless of the scavenger used. In our work, we have found that Pd scavenging after the Heck reaction is much less efficient over Pd^0/SiO_2 than over $Pd(acac)_2$ using an identical scavenger. It is admitted that the factors affecting the metal scavenging efficiency are multiple and complicated besides the nature of the functional groups on a scavenger.[26,36,41] Even by using excellent scavengers such as SH-MCM-41 and SH-SiO_2, much of the leached Pd cannot be removed from solution during the Heck reaction over Pd^0/SiO_2 and the amount of leached soluble Pd cannot decrease with the scavenging time (Table 4 and Supporting Information). The remaining soluble Pd is deemed to contain predominantly Pd clusters because nearly all free molecular Pd^0 is scavenged in the presence of SH-silica and the resulting Pd−S bound to silica is hardly leached into solution. Therefore, we believe that the metal scavenging efficiency depends importantly on the nature of the soluble metal. The higher the proportion of metal clusters, the lower would be the metal scavenging efficiency. While in C−C coupling reactions, soluble Pd^{II} is naturally converted to soluble molecular Pd^0 and Pd clusters. The different solvents and temperatures used in C−C coupling reactions may possibly produce the different proportions of Pd clusters that are reflected in the different levels of remaining Pd residues after Pd scavenging in a reported study.[36] Using different Pd precatalysts (Pd compound/supported Pd particles) in a Heck reaction leads to different proportions of Pd clusters.[15] The much lower efficiency of Pd scavenging from solution over Pd^0/SiO_2 than over $Pd(acac)_2$ may be due to the much higher fraction of Pd clusters in solution over Pd^0/SiO_2 than over $Pd(acac)_2$. We have recently demonstrated that the presence of supported Pd particles promotes the growth of soluble Pd clusters during the Heck reaction, which results in a dominant proportion of Pd clusters in the soluble Pd species.[15] Evidently, the persistence of soluble Pd clusters with such an effective scavenger questions whether solid-bound ligand scavengers are capable of coping with metal clusters. Our analytical results suggest that solid-bound ligands can hardly scavenge Pd clusters from solution. An explanation for this may be tentatively made in terms of the steric effect of the solid surface upon complexation between an immobilized ligand and a Pd cluster. Although both molecular Pd and Pd clusters can be strongly complexed with free thiol and amine ligands in solution,[90−94] the Pd cluster dimension and the steric barrier between a solid-immobilized ligand and a Pd cluster may render complexation unavailable.[92] The ability of solid-bound ligands to remove Pd clusters ought to allow for both the sufficient number of ligands to complex a Pd cluster and the sufficient geometric space that a Pd cluster needs around solid-bound ligands.

Between MPA and SH-silica, MPA has a stronger ability to scavenge soluble molecular Pd^0 leached from Pd^0/SiO_2 under Heck reaction conditions unless thiol leaching into solution takes place. Before the bound thiols are leached into solution from the solid phase (within 10 min of Pd scavenging), MPA is significantly more efficient than SH-silica in Pd scavenging. After the bound thiols have been leached into solution from Pd^0/SiO_2 + MPA, the Pd scavenging efficiency of MPA decreases because of the appearance of much more Pd−S in solution. In contrast, the thiols bound to silica are much more stable so that much less Pd−S is produced in solution and the Pd scavenging efficiency of SH-silica remains more stable. Between MPA and SH-silica, the relative ability to scavenge soluble molecular Pd^0 over Pd^0/SiO_2 is actually consistent with that found over $Pd(acac)_2$ during the Heck reaction. Because of the production of considerable amounts of Pd−S in solution, which inhibits the Pd scavenging by MPA, SH-silica has an obvious advantage in Pd scavenging from solution. At temperatures from 90 °C upward, the pore structure of polymer resin is supposed to have sufficiently swelled to allow Pd or Pd compound diffusion into the polymer matrix.[8,49] In the present work, the following facts have been observed. First, the catalytic activity in the Heck coupling of PhBr and styrene over $Pd(acac)_2$ or Pd^0/SiO_2 is quenched upon poisoning with MPA at 90 or 135 °C. Second, the Pd scavenging efficiency ranks with varying soluble Pd species in the order of metallic Pd > $Pd(acac)_2$ > palladium acetate at 135 °C when using either MPA or SH-SiO_2 as the scavenger. Third, the scavenging efficiency of palladium acetate having the greater steric barrier on Pd^{II} increases gradually with the scavenging time when using either MPA or SH-SiO_2 as the scavenger, although it is much lower than those of metallic Pd and $Pd(acac)_2$. These facts suggest that the thiol ligands on the polymer matrix of MPA are made sufficiently accessible to either dissolved metallic Pd or dissolved Pd compound under the conditions used here as in the case with SH-SiO_2.

Behind the observed higher concentrations of soluble Pd residues during Pd scavenging, the serious loss of Pd from Pd^0/SiO_2 is accompanied by leaching of the functional groups from the scavengers to different extents under the conditions used here. We believe that the apparent interaction between the scavenger and the supported Pd particles takes place under the reaction conditions. The direct interaction of thiols on the scavengers with the vast majority of the Pd particles that are supported on the internal surface of SiO_2 is unlikely.[43,45,47] However, the indirect interaction can be envisioned via leaching of bound thiols, on the one hand, although no information is available, and via leaching of the supported Pd particles, on the other hand. According to our EA and TGA data, all of the scavengers studied here are likely to have the thiol leaching behavior in the Heck reactions at temperatures as low as 90 °C. The liberated thiols can freely access the pores of SiO_2 to interact with the supported Pd particles, as well as the solution to react with soluble Pd. If possible active sites of supported Pd particles are likewise poisoned, the experimental results will be clouded and selective poisoning will be trivial. In an assessment of the nature of the true active species, the use of only a single method may lead to incorrect conclusions. Especially without analytical data, positive results from catalyst poisoning by solid-bound ligands are not necessarily sufficient proof for ruling out the possibility of catalysis of solid Pd when C−C coupling reactions with solid Pd precatalysts are probed. Therefore, different methods should be integrated with each other to gain a correct picture of the overall catalysis in a solid−liquid system.[1,4] Through a study of the dependence of the reaction rate on Pd loading and on the leached Pd concentration, we have recently demonstrated that the leached soluble Pd is solely responsible for catalysis irrespectively of the supported Pd particles in the Heck coupling of PhBr and styrene over an identical precatalyst Pd^0/SiO_2.[15] This provides an important proof that the supported Pd particles do not contribute to catalysis. Only on this basis can catalyst poisoning by solid-bound ligands be convincingly conducted to determine the nature of the true active Pd species.

Behavior of Soluble Pd Species Leached from Pd^0/SiO_2. In light of the poisoning effect of the scavengers on catalysis for the Heck reaction over Pd^0/SiO_2, all of the existing catalytic active species including soluble active Pd species are completely deactivated after the addition of any of the scavengers as described above. In such a system, soluble active Pd has been scavenged and soluble inactive Pd consists of Pd clusters and Pd—S. In order to shed light on the different soluble Pd species with distinct properties due to interaction between the scavenger and Pd^0/SiO_2, we next shifted our concern to the behavior of soluble Pd species. The use of effective scavengers allows soluble inactive Pd to be in situ isolated from soluble active Pd for accurate studies. We have recently reported the behavior of active Pd species in a soluble Pd mixture.[15] The present study will help to gain a further understanding of the true active Pd species in leached soluble Pd by commonly used experimental methods.

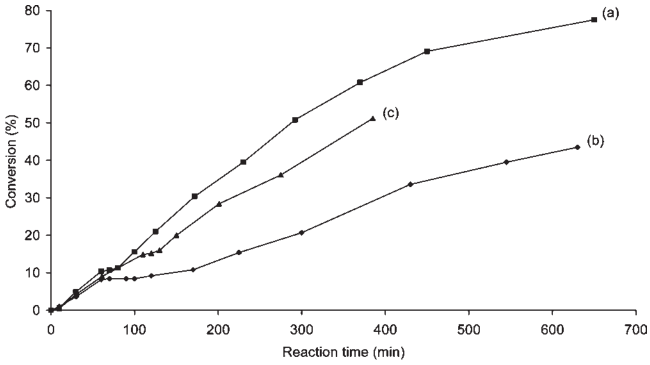


Figure 11. Heck coupling profiles of PhBr and styrene over Pd^0/SiO_2 in the presence of Na_2CO_3 at 135 °C for (a) 60 min and then 10 min after the addition of MPA followed by filtration testing, (b) 60 min and then 30 min after the addition of MPA followed by filtration testing, and (c) 110 min and then 10 min after the addition of MPA followed by filtration testing.

Figures 11—16 show the filtration test results and the TEM observations of soluble inactive Pd species after catalyst poisoning in the Heck reaction over Pd^0/SiO_2. In a first array of filtration tests, Heck reactions were performed in the presence of Na_2CO_3 over Pd^0/SiO_2 at 135 °C under Ar to 60 min followed by the addition of a scavenger. The poisoned systems were further stirred at 135 °C under Ar for a time before filtration testing. The result depended naturally on the scavenger used and the poisoning time. In the case with MPA used as the scavenger, the filtrate after 10 min of poisoning exhibited a much higher activity than the Pd^0/SiO_2 system (Figure 11a), while the filtrate after 30 min of poisoning displayed an activity comparable to that of the Pd^0/SiO_2 system (Figure 11b). The former result may be interpreted by the assumption that free molecular Pd^0 is produced from Pd clusters through the equilibrium shift in the absence of thiol ligands in the filtrate, which is consistent with the known behavior of the filtrate from the Pd^0/SiO_2 system without a scavenger.[15,21] It may reflect that the solution contains Pd clusters as the only soluble Pd and no thiol ligands after 10 min of poisoning, in accordance with the analytical results. In the presence of MPA, free molecular Pd^0 in the equilibrium is completely scavenged by the solid-bound thiols so that the activity of the system is naturally extinguished. The latter result may be explained by the possibility that most of the free molecular Pd^0 produced by the equilibrium shift is complexed with the leached thiols to form Pd—S in the filtrate. It may imply that the solution comprises Pd clusters, Pd—S, and considerable amounts of leached thiols after 30 min of poisoning, which is also consistent with the analytical results. To reason the decreased activity in the latter case with respect to the former case, we ran

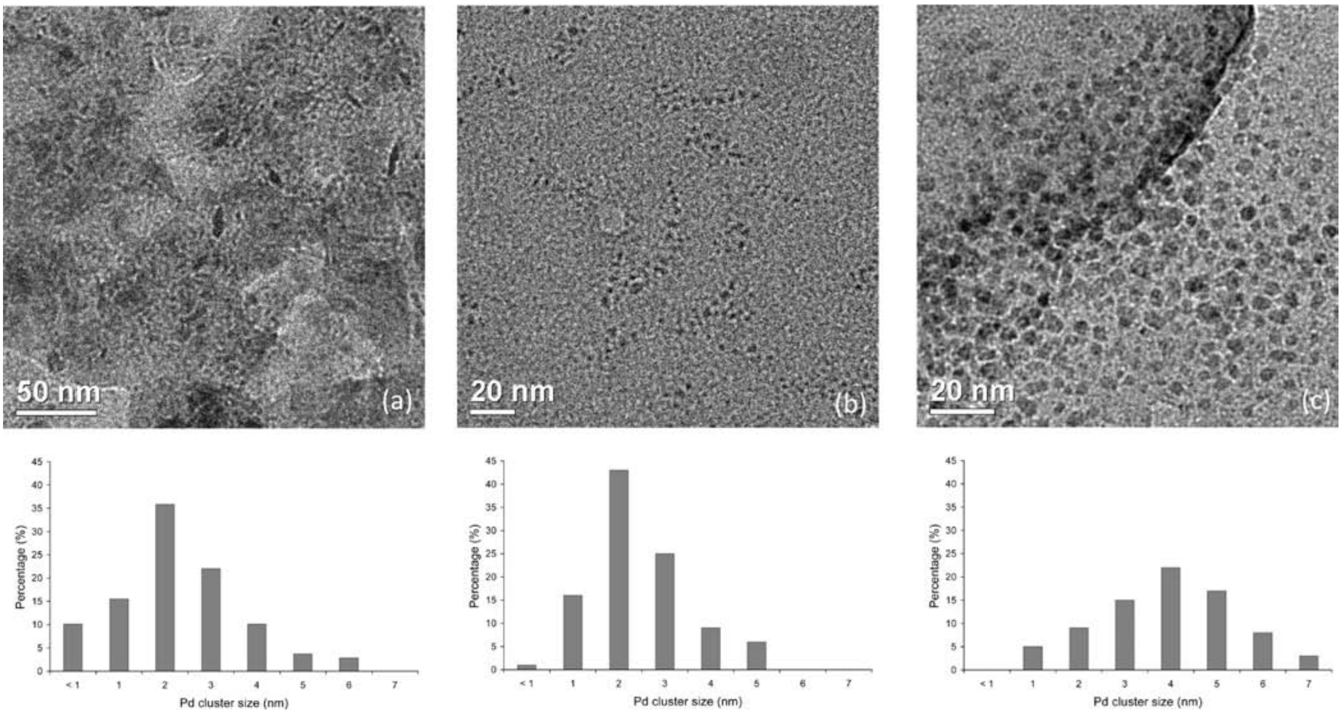


Figure 12. TEM images and Pd cluster size distributions of the samples from the reaction solution after the Heck coupling of PhBr and styrene over Pd^0/SiO_2 in the presence of Na_2CO_3 at 135 °C for (a) 60 min, (b) 60 min followed by 10 min of poisoning with MPA, and (c) 60 min followed by 30 min of poisoning with MPA.

an additional Heck reaction up to 110 min before adding MPA. The filtrate after 10 min of poisoning showed a slightly lower activity (Figure 11c) than that in the former case (Figure 11a). This shows that a longer interaction between soluble Pd and supported Pd particles affects the activity of the filtrate only to a limited extent, agreeing with our recent report.[15]

The persistence of Pd clusters in solution after catalyst poisoning is substantiated by TEM, as shown in Figure 12. Although soluble Pd was subjected to poisoning treatment with MPA and its catalytic activity was shut down, Pd clusters were still observed in TEM images and confirmed by EDX, which is consistent with the EA results. At the same time, the promotion of MPA on the upward shift of the soluble Pd cluster size distribution is displayed. After 10 min of poisoning, the soluble Pd cluster size distribution remained basically unchanged except a fall for the percentage of Pd clusters smaller than 1 nm. At this point, 29.5% soluble Pd is scavenged, as shown in Table 4. This significant change in the soluble Pd amount is almost not accompanied by a change in the soluble Pd cluster size distribution, which postulates that only molecular Pd^0 and Pd clusters smaller than 1 nm are scavenged from the solution with MPA, as in the case of Pd scavenging in the Heck reaction over $Pd(acac)_2$ described previously herein and in the Supporting Information. After 30 min of poisoning, the soluble Pd cluster size distribution shifted upward obviously with the disappearance of Pd clusters smaller than 1 nm. We assess that Pd clusters from 1 nm upward in size are not scavenged with MPA from solution during this 20 min period. In our recent study, a slow upward shift of the soluble Pd cluster size distribution was observed in the Heck reaction over Pd^0/SiO_2, which is attributed to the promoting effect of supported Pd particles on the aggregation of leached soluble Pd.[15] Probably via rapid leaching and aggregation of molecular Pd species under a promotional condition, smaller supported Pd particles and smaller Pd clusters shrink more rapidly in favor of the growth of larger supported Pd particles and larger Pd clusters, respectively.[15,87,95−97] In the copresence of MPA and Pd^0/SiO_2, the upward shift is markedly faster. This is likely related to the impact of MPA on the aggregation of leached soluble Pd via complexation with leached Pd. The high Pd loss from Pd^0/SiO_2, the high Pd leaching into solution, and full deactivation in the presence of MPA have shown that MPA and MPA-leached thiols complex strongly leached molecular Pd^0 to form Pd-MPA and Pd−S, respectively. Such complexation may possibly promote the growth of soluble larger Pd clusters while speeding up Pd leaching into solution from the supported Pd particles. In the meantime, soluble smaller Pd clusters may shrink more rapidly because of dissociation of Pd atoms accelerated by such complexation. The TEM measurements afford quasi-quantitative evidence that the soluble Pd clusters even as small as 1 nm are inactive for the Heck reaction as well as being unable to be complexed by MPA because of the steric factor. On the other hand, the upward shift of the soluble Pd cluster size distribution with the promoting effect of MPA supports the mechanism of Pd leaching from Pd^0/SiO_2 + MPA during the Heck reaction depicted in Scheme 1.

In the case with SH-MCM-41 or SH-SiO_2 used as the scavenger, the filtrate after catalyst poisoning behaved similarly to the case with MPA. As shown in Figure 13, the filtrate exhibited a high activity after 10 min of poisoning and a low activity after 30 min of poisoning. The results further suggest that the solution contains predominantly Pd clusters at the initial poisoning stage and that leached thiols enter progressively into solution during poisoning, consistent with the analytical data. It seemed that after 30 min of poisoning the thiol leaching into solution reached such an extent that free molecular Pd^0 dissociated from Pd clusters could be mostly complexed to form Pd−S. Likewise, Pd clusters persisted in solution after catalyst poisoning, as evidenced by TEM−EDX. Similar to when MPA was used, Pd clusters smaller than 1 nm were removed from solution with SH-MCM-41 and the upward shift of the soluble Pd cluster size distribution was enhanced in the presence of SH-MCM-41, as shown in Figure 14. SH-silica is assumed not to scavenge soluble Pd clusters from 1 nm upward in size, based on the fact that the percentage of soluble Pd clusters of 1 nm in size is not reduced after 60 min of poisoning. The upward shift of the soluble Pd cluster size distribution should be primarily promoted by SH-MCM-41, which is consistent with the related Pd leaching from Pd^0/SiO_2 during Pd scavenging and catalyst poisoning with SH-MCM-41 illustrated in Scheme 2.

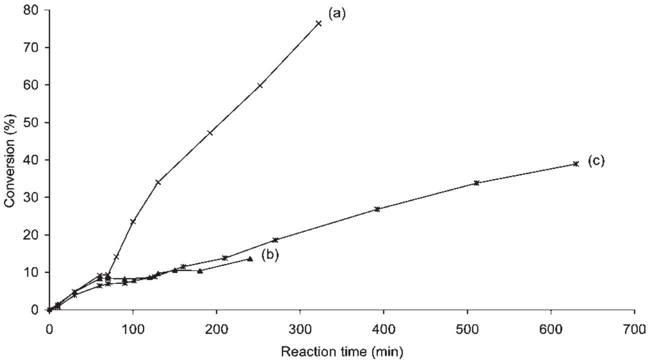


Figure 13. Heck coupling profiles of PhBr and styrene over Pd^0/SiO_2 in the presence of Na_2CO_3 at 135 °C for 60 min and then (a) 10 min after the addition of SH-MCM-41 followed by filtration testing, (b) 60 min after the addition of SH-MCM-41 followed by filtration testing, and (c) 30 min after the addition of SH-SiO_2 followed by filtration testing.

In light of the catalyst poisoning and filtration test results together with the TEM observations of soluble inactive Pd, the question about whether soluble Pd clusters are also active in the Heck reaction studied seems unnecessary. Although leached thiols can poison Pd clusters as well as free molecular Pd^0 and supported Pd particles, thiol leaching into solution from the solid phase is absent within 10 min after the addition of any of the scavengers to the reaction system with Pd^0/SiO_2 at 90 and 135 °C. The extinction of catalysis over Pd^0/SiO_2 and the persistence of Pd clusters in solution with the presence of any of the scavengers have significantly demonstrated that soluble unpoisoned Pd clusters are inactive. At least, the activity of soluble Pd clusters for the Heck reaction has not been observed under the technical conditions used here. The emergence of marked catalysis in solution without the presence of a scavenger has clearly demonstrated that free molecular Pd^0 in solution is solely active. Even if the possibility of poisoning of soluble Pd clusters by undetectable amounts of leached thiols existed, the activity of soluble unpoisoned Pd clusters would be incomparable to that of free molecular Pd^0, and the homogeneous nature of catalysis would not be affected.

In a second array of filtration tests, Heck reactions were conducted in the presence of NaOAc over Pd^0/SiO_2, Pd^0/SiO_2 + MPA, or Pd^{II}/MPA at 135 °C under Ar to 60 min before filtration testing. Except that the amount of either Pd^0/SiO_2 or the scavenger was increased to 0.15 g, the other reaction

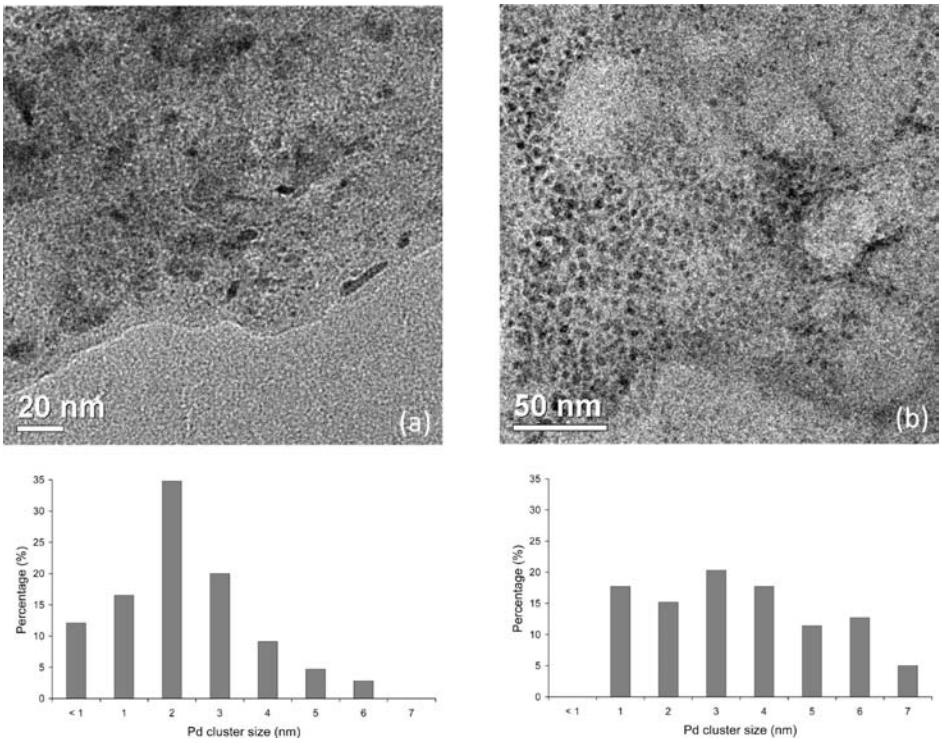


Figure 14. TEM images and Pd cluster size distributions of the samples from the reaction solution after the Heck coupling of PhBr and styrene over Pd^0/SiO_2 in the presence of Na_2CO_3 at 135 °C for (a) 60 min and (b) 60 min followed by 60 min of poisoning with SH-MCM-41.

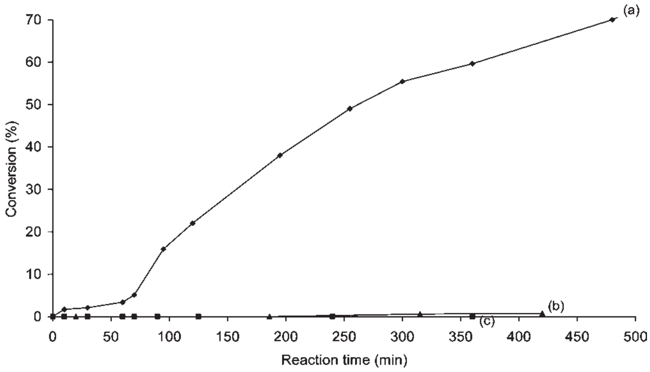


Figure 15. Heck coupling profiles of PhBr and styrene in the presence of NaOAc at 135 °C over (a) Pd^0/SiO_2 for 60 min followed by filtration testing, (b) Pd^0/SiO_2 + MPA for 60 min followed by filtration testing, and (c) Pd^{II}/MPA for 60 min followed by filtration testing.

conditions remained identical. This array of experiments aimed to elucidate the effects of the copresence of a scavenger and leached Pd throughout the Heck reaction on the composition of inactive Pd and on the distribution of Pd cluster sizes in solution. As seen in Figure 15, the activity of the filtrate was quite high in the case of Pd^0/SiO_2 as expected,[15,21] whereas those of the filtrates were negligible and null in the cases with Pd^0/SiO_2 + MPA and with Pd^{II}/MPA, respectively. Meanwhile, Pd cluster size distributions of the filtrates centered at 1−2 nm were observed by TEM−EDX after 60 min of the Heck reaction, as shown in Figure 16. In the case with Pd^0/SiO_2 alone, Pd clusters around 1 nm and smaller in size dominated, whereas in the case with Pd^0/SiO_2 + MPA, the Pd cluster size distribution shifted upward significantly. This confirms the promoting effect of MPA on the upward shift of the soluble Pd cluster size distribution during the Heck reaction over Pd^0/SiO_2. The TEM−EDX observations indicate that Pd clusters can be produced in solution via Pd leaching despite the copresence of MPA and Pd^0/SiO_2 from the very beginning of the Heck reaction. According to the TEM−EDX and analytical results, the filtrate comprises definitely Pd clusters, Pd−S, and leached thiols in the case with Pd^0/SiO_2 + MPA. The negligible activity of the filtrate is in accordance with serious thiol leaching into solution from MPA, which nearly avoids the production of free molecular Pd^0. The presence of MPA diminished markedly but failed to get rid of Pd clusters smaller than 1 nm. In the case with Pd^{II}/MPA, no Pd clusters were observed by TEM−EDX (Supporting Information). This is well consistent with the catalytic inactivity over the filtrate or Pd^{II}/MPA. Pd clusters are the unique catalyst precursor in solution that can breed the active species under the conditions used, as discussed previously herein.

This study further suggests by simpler methods that free molecular Pd^0 acts solely as the true catalytic species for Heck reactions irrespective of Pd clusters. Quite a number of studies have proposed the "homogeneous" nature of leached soluble Pd catalysts in C−C coupling reactions with supported Pd particles,[1,7−9,15,98−107] only a couple of which provide powerful proof, e.g., through catalyst poisoning, kinetic testing, filtration testing, and three-phase testing.[8,15,101] The only study on the distinction between molecular Pd and Pd clusters in catalysis for C−C coupling reactions has been reported by Gaikwad et al., who demonstrated by membrane separation that catalysis for Heck and Suzuki reactions over Pd clusters involves molecular Pd species released from the surface of the clusters rather than the clusters as the active species.[6]

With regards to the assessment of the nature of catalysis for metal-catalyzed reactions, it is worth emphasizing that the conclusion should be based on the relative activity of soluble

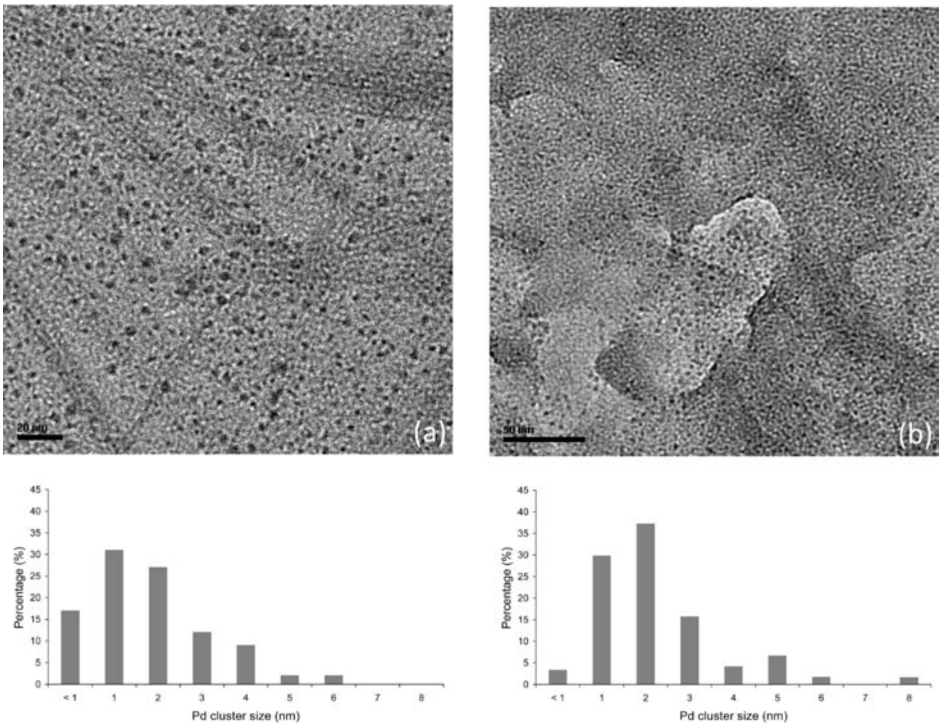


Figure 16. TEM images and Pd cluster size distributions of the samples from the reaction solution after the Heck coupling of PhBr and styrene in the presence of NaOAc at 135 °C over (a) Pd^0/SiO_2 for 60 min and (b) Pd^0/SiO_2 + MPA for 60 min.

molecular metal to soluble metal clusters and/or solid metal particles for the reaction studied. In the present work, it is because the activity of molecular Pd is solely observed without that of Pd clusters and SiO_2-supported Pd particles that the homogeneous nature of catalysis is suggested. Even if the activity of soluble metal clusters and/or solid metal particles is observed to be insignificant with respect to that of soluble molecular metal, the homogeneous nature of catalysis remains. However, if soluble metal clusters and/or solid metal particles are observed to dominate activity, then the heterogeneous nature of catalysis is postulated.

CONCLUSIONS

The following conclusions can be drawn from the results obtained in this work:

(1) Silica-bound thiol scavengers such as SH-SiO_2 and SH-MCM-41 are more efficient than resin-bound thiol scavengers such as MPA in residual Pd removal from the Heck reaction solution under the conditions used here. The efficiency of Pd compound scavenging from solution is dependent on the property of the solvents. In a given solvent, the efficiency of Pd scavenging relies on the effectiveness of solid-bound thiol binding to Pd. The steric barrier of Pd^{II} in a Pd compound leads to a low efficiency of Pd removal with the scavengers. Pd scavenging is highly improved after the Pd compound has been treated under Heck reaction conditions to give soluble Pd^0.

(2) The use of MPA, SH-SiO_2, and SH-MCM-41 poisons efficiently the catalytic species for the Heck coupling of PhBr and styrene either over Pd^0/SiO_2 or over $Pd(acac)_2$. However, successful catalyst poisoning does not necessarily imply an effective Pd scavenging from solution. Soluble Pd residues are hardly removed by the scavengers during or after the Heck reaction. Presumably because of the steric factor affecting the complexation between solid-immobilized ligand and Pd cluster, only molecular Pd^0 and Pd clusters smaller than 1 nm can be scavenged from solution with the scavengers.

(3) Because of a small proportion of soluble Pd clusters, Pd scavenging over $Pd(acac)_2$ is much more efficient than that over Pd^0/SiO_2 under the Heck reaction conditions used here.

(4) With the catalytic species poisoned by any of the scavengers, soluble Pd clusters, even if very small in size, are justified to be inactive for the Heck coupling of PhBr and styrene. Soluble molecular Pd^0 is deemed to act solely as the true active species in the Heck reaction over Pd^0/SiO_2, which clearly disagrees with the results of Jana et al. about the heterogeneous nature of catalysis in Heck and Sonogashira couplings over their Pd^0/MCM-41.[28]

(5) The bound thiol leaching from the scavengers occurs more or less during the Heck coupling of PhBr and styrene at 135 °C, even at 90 °C, probably because of base-catalyzed decomposition of the functional groups from MPA and base-promoted dissociation of the functional groups from silica. When the scavengers are applied to the Heck reaction system with Pd^0/SiO_2, leached thiols likely access the pores of SiO_2 to interact with the supported Pd particles as well as the solution to react with soluble Pd. The scavengers play a promotional role in Pd leaching from Pd^0/SiO_2 and the upward shift of the soluble Pd cluster size distribution via complexation with leached Pd.

(6) Under the Heck reaction conditions used here, resin-bound thiol scavengers like MPA leach many more thiols

than silica-bound thiol scavengers. The use of the former results in a large amount of soluble Pd containing mostly Pd−S, whereas the use of the latter produces a small amount of soluble Pd comprising primarily Pd clusters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Supplementary results of Pd ICP calibration, solubility data of Na_2CO_3 and NaOAc in DMA at 135 °C, most of the TGA data of MPA and SH-silica before and after Pd scavenging, supplementary Pd leaching into solution profiles during a Heck reaction over (Pd^0/SiO_2 + scavenger) and over Pd^{II}/scavenger at 135 °C, results of Pd scavenging and catalyst poisoning over Pd^0/SiO_2 at 90 °C, TEM images and Pd cluster size distributions of the samples from the reaction solution with $Pd(acac)_2$ before and after Pd scavenging, and TEM-EDX evidence for the absence of Pd clusters in the reaction solution after a Heck reaction over Pd^{II}/MPA at 135 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: huang_lin@ices.a-star.edu.sg. Tel: (+65)-6796-3831. Fax: (+65)-6316-6182.

■ ACKNOWLEDGMENT

This project was supported by the Agency for Science, Technology and Research (A*STAR), Singapore.

■ REFERENCES

(1) Phan, N. T. S.; van der Sluys, M.; Jones, Ch. W. *Adv. Synth. Catal.* **2006**, *348*, 609 and references cited therein.

(2) Polshettiwar, V.; Molnár, Á. *Tetrahedron* **2007**, *63*, 6949.

(3) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302.

(4) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.

(5) Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2886.

(6) Gaikwad, A. V.; Holuigue, A.; Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. *Chem.—Eur. J.* **2007**, *13*, 6908.

(7) Chen, J.-S.; Vasiliev, A. N.; Panarello, A. P.; Khinast, J. G. *Appl. Catal., A* **2007**, *325*, 76.

(8) Richardson, J. M.; Jones, Ch. W. *J. Catal.* **2007**, *251*, 80.

(9) Trzeciak, A. M.; Ziólkowski, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1281.

(10) Coelho, A. C.; de Souza, A. L. F.; De Lima, P. G.; Wardell, J. L.; Antunes, O. A. C. *Tetrahedron Lett.* **2007**, *48*, 7671.

(11) Simeone, J. P.; Sowa, H. R. *Tetrahrdron* **2007**, *63*, 12646.

(12) Diallo, A. K.; Ornelas, C.; Salmon, L.; Aranzaes, J. R.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644.

(13) Diéguez, M.; Pàmies, O.; Mata, Y.; Teuma, E.; Gómez, M.; Ribaudo, F.; van Leeuwen, P. W. N. M. *Adv. Synth. Catal.* **2008**, *350*, 2583.

(14) Köhler, K.; Heidenreich, R. G.; Soomro, S. S.; Pröckl, S. S. *Adv. Synth. Catal.* **2008**, *350*, 2930.

(15) Huang, L.; Wong, P. K.; Tan, J.; Ang, T. P.; Wang, Z. *J. Phys. Chem. C* **2009**, *113*, 10120.

(16) Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262.

(17) Handa, P.; Wikander, K.; Holmberg, K. *Microporous Mesoporous Mater.* **2009**, *117*, 126.

(18) Bernechea, M.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. *Inorg. Chem.* **2009**, *48*, 4491.

(19) Joucla, L.; Cusati, G.; Pinnel, C.; Djakovitch, L. *Appl. Catal., A* **2009**, *360*, 145.

(20) Amoroso, F.; Colussi, S.; Zotto, A. D.; Llorca, J.; Trovarelli, A. *J. Mol. Catal. A: Chem.* **2010**, *315*, 197.

(21) Huang, L.; Tan, J.; Wong, P. K. *Chem. Today* **2010**, *28*, 29.

(22) Klingelhöfer, S.; Heitz, W.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116.

(23) Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. G. *Langmuir* **1999**, *15*, 7621.

(24) Dans, M.; Drijkomingen, L.; Pauvels, B.; van Tendeloo, G.; de Vos, D. E.; Jacob, P. A. *J. Catal.* **2002**, *209*, 225.

(25) Narayanan, R.; Tabor, C.; El-Sayed, M. *J. Phys. Chem. B* **2004**, *108*, 8572.

(26) Crudden, C. M.; Sateesh, M.; Lewis, R. *J. Am. Chem. Soc.* **2005**, *127*, 10045.

(27) Webb, J. D.; MacQuarrie, S.; McEleney, K.; Crudden, C. M. *J. Catal.* **2007**, *252*, 97.

(28) Jana, S.; Dutta, B.; Bera, R.; Koner, S. *Inorg. Chem.* **2008**, *47*, 5512.

(29) Tsvelikhovsky, D.; Popov, I.; Gutkin, V.; Rozin, A.; Shvartsman, A.; Blum, J. *Eur. J. Org. Chem.* **2009**, 98.

(30) Wan, Y.; Wang, H.; Zhao, Q.; Klingstedt, M.; Terasaki, O.; Zhao, D. *J. Am. Chem. Soc.* **2009**, *131*, 4541.

(31) Ellis, P. J.; Fairlamb, I. J. S.; Hackett, S. F. J.; Wilson, K.; Lee, A. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1820.

(32) Gruber, A. S.; Pozebon, D.; Monteiro, A. L.; Dupont, J. *Tetrahedron Lett.* **2001**, *42*, 7345.

(33) Rouhi, A. M. *Chem. Eng. News* **2004**, *82*, 49.

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

(35) Garrett, C. E.; Prasad, K. *Adv. Synth. Catal.* **2004**, *346*, 889.

(36) Galaffu, N.; Man, S. P.; Wilkes, R. D.; Wilson, J. R. H. *Org. Process Res. Dev.* **2007**, *11*, 406.

(37) Nikbin, N.; Ladlow, M.; Ley, S. V. *Org. Process Res. Dev.* **2007**, *11*, 458.

(38) Pink, Ch. J.; Wong, H-t.; Ferreira, F. C.; Livingston, A. G. *Org. Process Res. Dev.* **2008**, *12*, 589.

(39) Ishihara, K.; Nakayama, M.; Kurihara, H.; Itoh, A.; Haraguchi, H. *Chem. Lett.* **2000**, 1218.

(40) Johnson Mattthey technical document.

(41) Kang, T.; Park, Y.; Yi, J. *Ind. Eng. Chem. Res.* **2004**, *43*, 1478.

(42) Sigma-Aldrich technical document.

(43) Yu, K.; Sommer, W.; Weck, M.; Jones, Ch. W. *J. Catal.* **2004**, *226*, 101.

(44) Sommer, W.; Yu, K.; Sears, J. S.; Ji, Y.; Zheng, X.; Davis, R. J.; Sherrill, C. D.; Jones, Ch. W.; Weck, M. *Organometallic* **2005**, *24*, 4351.

(45) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, Ch. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

(46) Caporusso, A. M.; Innocenti, P.; Aronica, L. A.; Vitulli, G.; Gallina, R.; Biffis, A.; Zecca, M.; Corain, B. *J. Catal.* **2005**, *234*, 1.

(47) Ji, Y.; Jain, S.; Davis, R. J. *J. Phys. Chem. B* **2005**, *109*, 17232.

(48) Parisien, M.; Valette, D.; Fagnou, K. *J. Org. Chem.* **2005**, *70*, 7578.

(49) Richardson, J. M.; Jones, Ch. W. *Adv. Synth. Catal.* **2006**, *348*, 1207.

(50) Aksin, Ö.; Türkmen, H.; Artok, L.; Cetinkaya, B.; Ni, C.; Büyükgüngör, O.; Özkal, E. *J. Organomet. Chem.* **2006**, *691*, 3027.

(51) Inés, B.; San Martin, R.; Moure, M. J.; Domínguez, E. *Adv. Synth. Catal.* **2009**, *351*, 2124.

(52) Snelders, D. J. M.; van Koten, G.; Gebbink, R. J. M. K. *J. Am. Chem. Soc.* **2009**, *131*, 11407.

(53) Richardson, J. M.; Jones, Ch. W. *J. Mol. Catal. A: Chem.* **2009**, *297*, 125.

(54) Demel, J.; Lamač, M.; Čejka, J.; Štěpnička, P. *ChemSusChem* **2009**, *2*, 442.

(55) Haeley, F. R. *Coord. Chem. Rev.* **1981**, *35*, 143.

(56) Wagner, M.; Köhler, K.; Djakovitch, L.; Weinkauf, S.; Hagen, V.; Muhler, M. *Top. Catal.* **2000**, *13*, 319.
(57) Köhler, K.; Wagner, M.; Djakovitch, L. *Catal. Today* **2001**, *66*, 105.
(58) Huang, L.; Wang, Z.; Ang, T. P.; Tan, J.; Wong, P. K. *Catal. Lett.* **2006**, *112*, 219.
(59) *Aldrichimica Acta* **2005**, *38*, 89.
(60) *ChemFiles* **2007**, *7*, Supplement 1.
(61) Jones, C. W.; Richardson, J. M. In *Catalysis of Organic Reactions*; Prunier, M. L., Ed.; CRC Press: Boca Raton, FL, 2009; p 193.
(62) Jorgensen, C. K. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, The Netherlands, 1968.
(63) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642.
(64) Trzeciak, A. M.; Ziólkowski, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1281.
(65) Xiong, Y.; Chen, J.; Wiley, B.; Xia, Y.; Yin, Y.; Li, Z.-Y. *Nano Lett.* **2005**, *5*, 1237.
(66) Chen, M.; Feng, Y.-g.; Wang, L.-y.; Zhang, L.; Zhang, J.-Y. *Colloids Surf., A* **2006**, *281*, 119.
(67) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.
(68) De Vries, A. H. M.; Mulders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285.
(69) Wu, H.-S.; Lee, C.-S. *J. Catal.* **2001**, *199*, 217.
(70) Skapski, A. C.; Smart, M. L. *J. Chem. Soc. D* **1970**, 658b.
(71) Romm, I. P.; Busiaeva, T. M.; Lyalina, N. N.; Shifrina, R. R.; Simitsyn, N. M. *Koord. Khim.* **1992**, *18*, 165.
(72) Bakhmutov, V. I.; Berry, J. F.; Cotton, F. A.; Ibragimov, S.; Murillo, C. A. *Dalton Trans.* **2005**, 1989.
(73) Fujimoto, K.; Yasuhiko, N.; Tadashi, T.; Taiseki, K. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 303.
(74) Hinchcliffe, A.; Hughes, C.; Pears, D. A.; Pitts, M. R. *Org. Process Res. Dev.* **2007**, *11*, 477.
(75) Zhang, Z.; Hirose, T.; Nishio, S.; Morioka, Y.; Azuma, N.; Ueno, A. *Ind. Eng. Chem. Res.* **1995**, *34*, 4514.
(76) Zhang, Z.; Nishio, S.; Morioka, Y.; Ueno, A.; Ohkita, H.; Tochihara, Y.; Mizushima, T.; Kakuta, N. *Catal. Today* **1996**, *29*, 303.
(77) Woo, O. S.; Ayala, N.; Broadbelt, L. J. *Catal. Today* **2000**, *55*, 161.
(78) Kim, J.-S.; Lee, W.-Y.; Lee, S.-B.; Kim, S.-B.; Choi, M.-J. *Catal. Today* **2003**, *87*, 59.
(79) Xie, C.; Liu, F.; Yu, S.; Xie, F.; Li, L.; Zhang, S.; Yang, J. *Catal. Commun.* **2008**, *9*, 1132.
(80) Blazsó, M. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 73.
(81) Xi, G.; Liang, R.; Tang, Q.; Li, J. *J. Appl. Polym. Sci.* **1999**, *78*, 1139.
(82) Kim, J.-S.; Lee, W.-Y.; Lee, S.-B.; Kim, S.-B.; Choi, M.-J. *Catal. Today* **2003**, *87*, 59.
(83) Lim, M. H.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1998**, *10*, 467.
(84) Margolese, D.; Melero, J. A.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2448.
(85) Tatsumi, T.; Koyano, K. A.; Tanaka, Y.; Nakata, S. *Chem. Lett.* **1997**, 469.
(86) Zhao, X. S.; Audsley, F.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 4143.
(87) Köhler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. *Chem.—Eur. J.* **2002**, *8*, 622.
(88) Urawa, Y.; Miyazawa, M.; Ozeki, N.; Ogura, K. *Org. Process Res. Dev.* **2003**, *7*, 191.
(89) Argonaut technical note 515, 2003, MP-TMT.
(90) Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; Rafailovich, M.; Sokolov, J. *Langmuir* **1999**, *15*, 3486.
(91) Chen, S.; Huang, K.; Stearns, J. A. *Chem. Mater.* **2000**, *12*, 540.
(92) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181.
(93) Quiros, I.; Yamada, M.; Kubo, K.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Langmuir* **2002**, *18*, 1413.
(94) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.
(95) Zhao, F.; Shirai, B. M.; Ikushima, Y.; Arai, M. *J. Mol. Catal. A: Chem.* **2002**, *180*, 211–219.
(96) Ratke, L.; Voorhees, P. W. *Growth and Coarsening: Ostwald Ripening in Material Processing*; Springer: Dordrecht, The Netherlands, 2002; p 117.
(97) Howard, A.; Mitchell, C. E. J.; Edgell, R. G. *Surf. Sci.* **2002**, *515*, L504.
(98) Coelho, A. C.; de Souza, A. L. F.; De Lima, P. G.; Wardell, J. L.; Antunes, O. A. C. *Tetrahedron Lett.* **2007**, *48*, 7671.
(99) Simeone, J. P.; Sowa, H. R. *Tetrahedron* **2007**, *63*, 12646.
(100) Diallo, A. K.; Ornelas, C.; Salmon, L.; Aranzaes, J. R.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644.
(101) Diéguez, M.; Pàmies, O.; Mata, Y.; Teuma, E.; Gómez, M.; Ribaudo, F.; van Leeuwen, P. W. N. M. *Adv. Synth. Catal.* **2008**, *350*, 2583.
(102) Köhler, K.; Heidenreich, R. G.; Soomro, S. S.; Pröckl, S. S. *Adv. Synth. Catal.* **2008**, *350*, 2930.
(103) Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Mülhaupt, R. *J. Am. Chem. Soc.* **2009**, *131*, 8262.
(104) Handa, P.; Wikander, K.; Holmberg, K. *Microporous Mesoporous Mater.* **2009**, *117*, 126.
(105) Bernechea, M.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. *Inorg. Chem.* **2009**, *48*, 4491.
(106) Joucla, L.; Cusati, G.; Pinnel, C.; Djakovitch, L. *Appl. Catal., A* **2009**, *360*, 145.
(107) Amoroso, F.; Colussi, S.; Zotto, A. D.; Llorca, J.; Trovarelli, A. *J. Mol. Catal. A: Chem.* **2010**, *315*, 197.