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Journal of Catalysis 227 (2004) 202–209
JOURNAL OF CATALYSIS
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Pd–sepiolite catalyst for Suzuki coupling reaction in water: Structural and catalytic investigations

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Received 24 May 2004; revised 6 July 2004; accepted 8 July 2004

Abstract

$[Pd(NH_3)_4]^{2+}$-exchanged sepiolite clay (Pd–sepiolite) has been applied to the catalytic Suzuki-type carbon–carbon coupling reactions of 4-bromophenol with phenylboronic acid or sodium tetraphenylborate in water. The Pd–sepiolite effectively catalyzed the reaction under mild reaction conditions (at room temperature in air). The Pd–sepiolite system exhibits higher yield than unsupported Pd(II) salts, $[Pd(NH_3)_4]Cl_2$-impregnated SiO_2 (Pd–SiO_2), and a commercially available Pd/C consisting of Pd metal particles. The structure of Pd species in the catalysts before and after the reaction was well characterized by a combination of XRD, TEM, UV-Vis, Pd K-edge XANES/EXAFS, and Pd L_{III}-edge XANES. XAFS and TEM results confirmed the formation of metal particles after the reaction by unsupported Pd(II) salt and Pd–SiO_2. In contrast, for Pd–sepiolite the change in the structure of Pd species after the reaction was not significant; the highly dispersed Pd(II) complex, present before the reaction, was still the main Pd species together with the small Pd clusters (2–7 nm) as minor species. As a result of the high stability, Pd–sepiolite was reused without losing its activity. Significantly high turnover numbers (TON = 940,000) were also attained at reflux temperature. It is suggested that Pd metal precipitation during the reaction is inhibited by a strong electrostatic interaction of sepiolite with Pd(II) species.

Keywords: Suzuki reaction; Palladium catalysts; Sepiolite; Water

1. Introduction

The palladium-catalyzed cross-coupling reaction of aryl halides and arylboronic acids (Suzuki reaction) is one of the most important methods for the preparation of biaryl compounds [1,2]. The reaction is normally carried out in organic solvents and catalyzed by homogeneous Pd catalysts with specific phosphine-based ligands [1–4]. However, homogeneous catalysts are generally connected with the problem of separation and wasted inorganics. The phosphine ligands and Pd precursors are usually difficult to handle because of their air-sensitive nature and are too difficult to reuse after the reaction. To solve these problems, it is highly desirable to develop phosphine-free heterogeneous catalysts that are recyclable and stable in air. From industrial and environmental points of view, the use of water as a safe and inexpensive solvent for Suzuki reaction is also desired, and several attempts have been focused on the Suzuki reaction in water [5–13].

Various supported Pd catalysts have been reported to be effective for Suzuki reaction [9–21], and a few heterogeneous catalysts can catalyze the Suzuki reaction in water [9–13]. Among them, amphiphilic polymer supported palladium catalysts [10] and oxime-carbapalladacycle anchored to silica [11] were shown to be highly active for the Suzuki reaction in water under an inert atmosphere. Pd/C was also shown to be effective for Suzuki reaction of iodophenols in water [13]. However, the reactivity and the stability of these

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doi:10.1016/j.jcat.2004.07.012

catalysts in air were not well studied, and a large amount of the catalysts were generally used for these heterogeneous catalytic systems whose turnover numbers were several orders of magnitude lower than those of the homogeneous catalysts. These aspects limit the industrial application of heterogeneous catalysts for Suzuki reaction.

The stability of the catalytic Pd species is also important for large-scale industrial applications of the coupling reactions. It is generally assumed that the deactivation of the Pd catalyst occurs via clustering of palladium intermediates in the catalytic cycle. It is well known that phosphine ligands stabilize Pd(0) intermediates and prevent the aggregation of them to inactive clusters [5–8,16]. The cation-exchangeable porous inorganic supports may be a candidate for the stabilizer of Pd(II) precursors and Pd(II) intermediates formed during the reaction. Indeed, $[Pd(NH_3)_4]^{2+}$-exchanged NaY zeolite has been shown to be effective for Heck [22,23] and Suzuki [15,17] reactions. For the Heck reaction, it was speculated that dissolved active Pd^0 species catalyze the reaction in the channels or cages by a homogeneous mechanism [22]. However, very little attention has been paid to the structural analysis of the active Pd species before and after the reaction [23], and hence the structure of the active Pd species during the reaction and the role of inorganic supports on the stabilization of Pd species are still speculatively discussed.

We chose a sepiolite as a support to stabilize the active Pd species. Sepiolite is an inexpensive natural clay mineral with ideal formula of $Mg_8Si_{12}O_{30}(OH)_4 \cdot 4H_2O \cdot nH_2O$. Its structure is formed of talc-like ribbons arranged in such a way that the tetrahedral sheet is continuous but inverts in apical directions in adjacent ribbons, generating uniform size parallel-piped intracrystalline tunnels (10.8 × 4.0 Å) along the fiber [24]. The magnesium ion on the tunnel wall can be substituted with various cations [25–27], and highly dispersed metal cations act as the catalytic active site [28–30]. Previously, we have reported preliminary results that the Pd–sepiolite catalyst is highly active and stable for Suzuki cross-coupling reactions of aryl bromides using DMF as a solvent at relatively high temperature under an inert atmosphere [20].

In this paper, we report that the Pd–sepiolite shows high TON for Suzuki-type coupling reactions in water. The catalyst is air stable and can be reused without noticeable loss of activity. The structure of the catalyst before and after the reaction is well characterized, and the results will be discussed to reveal the nature of the Pd species required for the stable catalysis in the Suzuki reaction in water.

2. Experimental

2.1. Catalyst preparation and characterization

According to our previous report [31], natural sepiolite (Konan, China) was treated with dilute HCl aqueous solution ($0.59\ \mathrm{mol\,dm^{-3}}$) to eliminate impurities (calcite and dolomite) without a decomposition of sepiolite itself. $[Pd(NH_3)_4]^{2+}$-exchanged sepiolite clay (Pd–sepiolite) was prepared by exchanging the sepiolite with an aqueous solution of $[Pd(NH_3)_4]Cl_2$ at 298 K for 48 h, followed by centrifuging and washing with deionized water, and subsequently drying in vacuo at 298 K. A similar procedure was used to prepare $[Pd(NH_3)_4]^{2+}$-exchanged NaY zeolite (Pd–NaY) and $[Pd(NH_3)_4]^{2+}$-exchanged mica (Pd–mica) using NaY (JRC-Z-Y 5.6, a reference catalyst of the Catalysis Society of Japan, $SiO_2/Al_2O_3 = 5.6$) and Na–mica (Na–fluorotetrasilicic mica, Somasif ME-100, with ideal formula of $NaMg_{2.5}Si_4O_{10}F_2$, COOP Chemicals Co. Ltd.), respectively. $[Pd(NH_3)_4]Cl_2$ dispersed on the amorphous silica ($Pd–SiO_2$) was prepared by an impregnation method, followed by drying in vacuo at 298 K.

XRD patterns were taken by MX Labo (MAC Science) with Cu$K\alpha$ radiation (40 kV, 25 mA). Diffuse reflectance spectra were obtained with a UV-Vis spectrometer (Jasco; V-550) and were converted from reflection to absorbance by the Kubelka-Munk method. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2010 operating at 200 kV. Pd K-edge XAFS spectra were taken at BL-10B of the Photon Factory in High Energy Accelerator Research Organization in Tsukuba (Japan), with a ring energy of 2.5 GeV and stored current of 250–350 mA. The spectra were recorded in a transmission mode at room temperature with a Si(311) channel-cut monochromator. The ionization chambers for I_0 (17 cm) and for I (31 cm) were filled with Ar. Pd L_{III} K-edge XANES (X-ray absorption near-edge structures) spectra were obtained at the BL-9A station of the Photon Factory with a ring energy of 2.5 GeV and a stored current of 250–350 mA. The spectra were recorded in a transmission mode at room temperature with a Si(111) double-crystal monochromator. High-energy X-rays from high-order reflections were removed by a pair of flat quartz mirrors coated with Rh/Ni that were aligned in parallel. The ionization chambers filled with N_2(30%)–He(70%) for I_0 (17 cm) and N_2(100%) for I (31 cm) were used. For Pd K and Pd L_{III} XAFS, the energy was defined by assigning the first inflection point of the Cu foil spectrum to 8980.3 eV.

2.2. Catalysts tested

The reagents were obtained from commercial sources and were used without further purification. A typical experimental procedure for Suzuki reactions is as follows. A 20-mL round-bottom flask was charged with 4-bromophenol (1 mmol) and phenylboronic acid (1.2 mmol) or sodium tetraphenylborate (0.27 mmol), Na_2CO_3 (3.0 mmol for phenylboronic acid or 1.75 mmol for sodium tetraphenylborate), catalyst (0.5 µmol, 0.05 mol% Pd), and 10 mL of water. The mixture was stirred at room temperature in air or in N_2. After the reaction, the basic solution was neutralized by dilute HCl solution, and products were extracted with ethyl acetate (3 mL) three times. After adding n-nonane as an internal standard in the organic phase, the product yield was determined by GC analysis. The product was identified based on the GC (comparison with commercial reagents) and ^{1}H NMR spectroscopy (JEOL NM-EXCALIBUR 270, $CDCl_3$ as solvent with TMS). For a large-scale experiment, a 1-L round-bottom flask was charged with 4-bromophenol (50 mmol) and phenylboronic acid (60 mmol), Na_2CO_3 (300 mmol), catalyst (0.0001 mol% Pd), and 500 mL of water. The mixture was stirred at a reflux temperature in air. After the reaction, the basic solution was neutralized by dilute HCl solution, and products were extracted with ethyl acetate. The organic phase was dried with $MgSO_4$ and evaporated under vacuum. The obtained white solid consisted of biphenyl-4-ol, and no side products were detected by GC and ^{1}H NMR analyses. For the catalyst characterization after the Suzuki-type reaction the used catalysts were prepared as follows; typically a mixture of 4-bromophenol (10 mmol), sodium tetraphenylborate (2.7 mmol), Na_2CO_3 (17.5 mmol), and the catalyst (1 mol% Pd) in 100 mL of water was stirred at room temperature for 5 h, followed by extracting the solid product with ethyl acetate, and by filtering and washing the solid catalyst with ethyl acetate and water, and by drying in vacuo at 298 K.

3. Results and discussion

3.1. Characterization of the as-prepared catalyst

ICP analysis of Pd–sepiolite showed that more than 95% of Pd^{2+} cations in the starting solution were exchanged on the support (Pd content = 0.5 wt%). XRD patterns of Pd–sepiolite were essentially the same as that of the sepiolite support. The surface area of Pd–sepiolite (240 $m^2\,g^{-1}$ by BET method) was very close to that of the original sepiolite (248 $m^2\,g^{-1}$). These results suggest that the palladium complex is immobilized on the surface of sepiolite, without changing its tunnel structure.

To clarify the nature of the Pd(II) species obtained by ion exchange with $[Pd(NH_3)_4]Cl_2$, UV-Vis and XAFS studies of Pd–sepiolite were performed. Fig. 1 shows UV-Vis diffuse-reflectance spectra of Pd–sepiolite and the sepiolite support. In the spectrum of Pd–sepiolite, a broad shoulder peak around 300–400 nm assignable to the *d–d* transition of Pd(II) species was observed. The position of the band is lower in energy than that for $[Pd(NH_3)_4]^{2+}$ in solution (295 nm) [32] and higher in energy than that for to the isolated Pd(II) ion coordinated to four framework oxygens of zeolites (O_Z) (around 300 nm) reported in the literature [33]. Jørgensen studied the effect of substitution of NH_3 ligands by H_2O and reported that the position of the *d–d* transition for $[Pd(NH_3)_2(H_2O)_2]^{2+}$ (341 nm) was higher in wavelength than $[Pd(NH_3)_4]^{2+}$ (295 nm) [32]. A similar shift in the band has been observed for $[Pd(NH_3)_4]^{2+}$-exchanged Na-Y zeolite calcined at low temperature (523 K) [33] and was due to the *cis*-$Pd^{2+}(NH_3)_2(O_Z)_2$. Therefore, the UV-Vis result suggests a substitution of several NH_3 ligands by the support oxygens possibly caused by the cation exchange at the pore wall of the sepiolite.

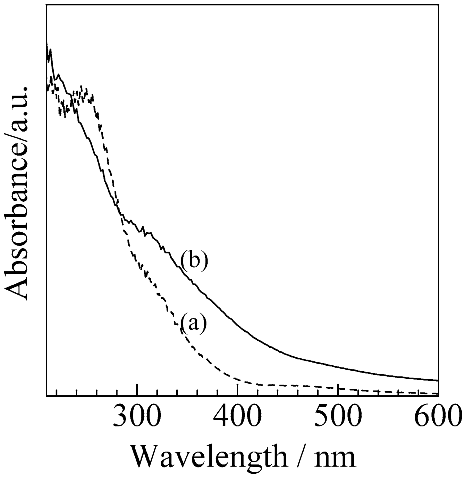


Fig. 1. UV-Vis spectra of (a) sepiolite and (b) Pd–sepiolite.

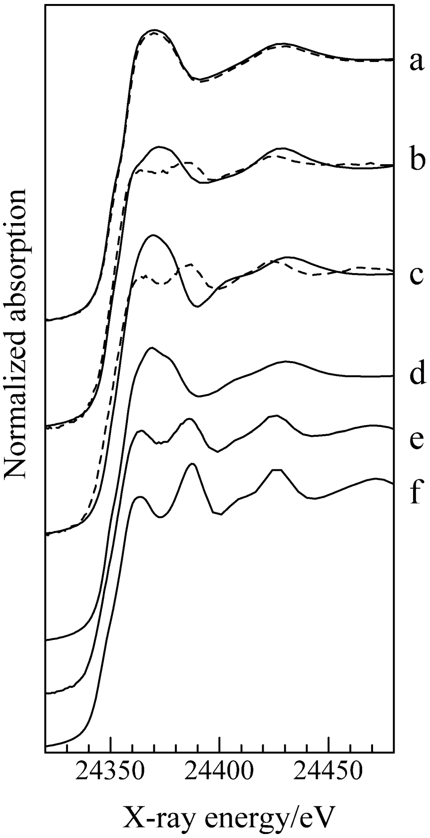


Fig. 2. Pd *K*-edge XANES spectra of (a) Pd–sepiolite, (b) Pd–SiO_2, (c) $Pd(OAc)_2$, (d) $[Pd(NH_3)_4]Cl_2$, (e) Pd/C, and (f) Pd foil. Dotted lines denote the spectra for the catalyst after the Suzuki reaction.

X-ray absorption near-edge structures around the Pd *K* edge for the fresh samples are shown in Fig. 2 (solid lines). The edge energy and XANES feature of Pd–sepiolite were close to those of Pd(II) salts, $[Pd(NH_3)_4]Cl_2$, and $Pd(OAc)_2$, indicating that Pd(II) species are supported on the sepio-

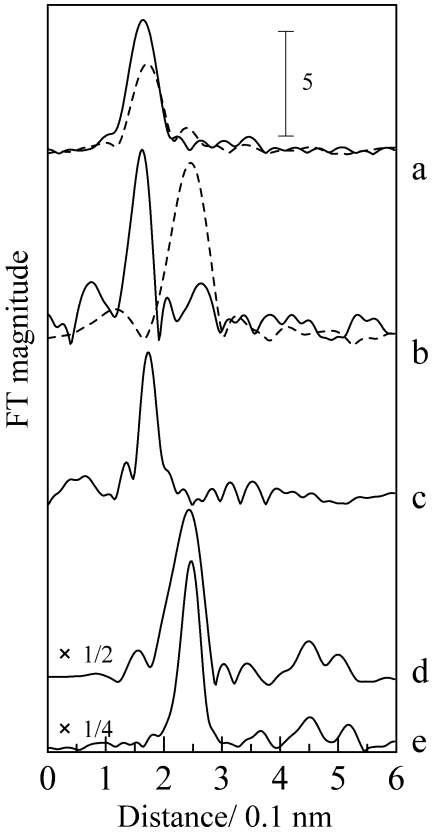


Fig. 3. Fourier transforms of k^3-weighted EXAFS spectra of (a) Pd–sepiolite, (b) $Pd(OAc)_2$, (c) $[Pd(NH_3)_4]Cl_2$, (d) Pd/C, and (e) Pd foil. Dotted lines denote the spectra for the catalyst after the Suzuki reaction.

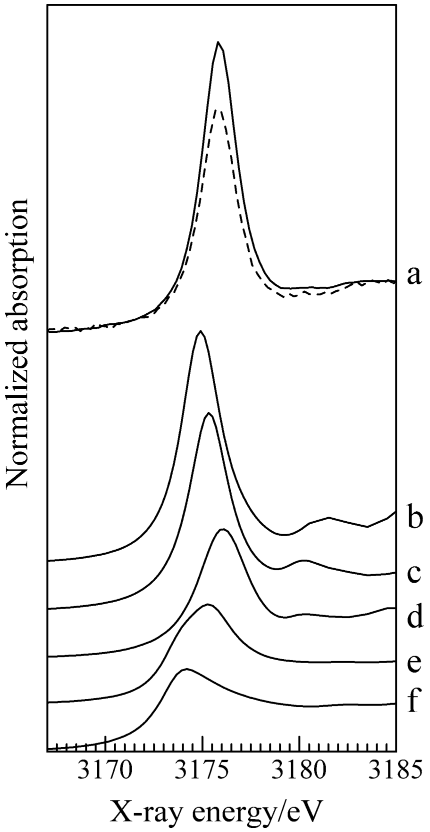
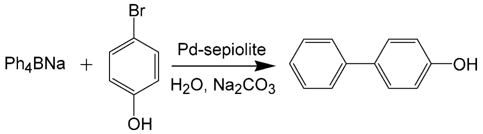


Fig. 4. Pd L_{III}-edge XANES spectra of (a) Pd–sepiolite, (b) $PdCl_2$, (c) $Pd(OAc)_2$, (d) $[Pd(NH_3)_4]Cl_2$, (e) Pd/C, and (f) Pd black. A dotted line denotes the spectrum for the Pd–sepiolite after the Suzuki reaction.

lite. Also, the edge energy and XANES feature of Pd–SiO_2 indicate that Pd(II) species are supported on the Pd–SiO_2 sample. Fig. 3 shows the Fourier transforms of k^3-weighted EXAFS spectra at the Pd K edge. Peaks centered around 0.16–0.17 nm (phase-shift uncorrected), observed on the spectra of Pd(II) salts, are due to the backscattering from the adjacent oxygen or nitrogen atoms. In the spectrum of Pd–sepiolite, a peak at 0.16 nm due to Pd–O and/or Pd–N is observed, and its EXAFS is featureless at higher distances, indicating that Pd(II) cations are highly dispersed in the sample. It should be noted that oxygen and nitrogen atoms are very similar as backscattering atoms, and thus we did not perform the curve-fitting analysis. A peak at 0.25 nm, which appears in the spectrum of Pd foil, indicates the presence of the second-neighboring Pd atom. In the spectrum of Pd/C, the peak due to the Pd–Pd shell (0.25 nm) is predominant, though its intensity is lower than that for Pd foil. The feature of Pd K-edge XANES of Pd/C is very close to that of Pd foil. These results indicate that small Pd particles are predominant Pd species on Pd/C. The presence of Pd metal particles on Pd/C was also confirmed by XRD; a very broad line around $2\theta = 40°$ due to Pd metal was observed (result not shown).

Pd L_{III}-edge XANES spectra of various Pd compounds and Pd–sepiolite are shown in Fig. 4. All the spectra exhibited a large white line peak centered around 3174.2–3176.0 eV. This peak can be assigned to the electronic transition from the Pd $2p_{3/2}$ to the unoccupied $4d$ states. In the spectra of Pd(II) compounds including Pd–sepiolite, a single symmetric absorption peak appears, and its shift in the energy is obvious. Within the square-planer Pd(II) complexes ($[Pd(NH_3)_4]Cl_2$, $Pd(OAc)_2$, and $PdCl_2$), the position of the peak shifts toward higher energy as the electronegativity of the bonding ligand decreases in the order N > O > Cl, or in other words, in the spectrochemical-series order ($NH_3 > OAc^- > Cl^-$). The same result was reported by Sugiura et al. [34], who proposed that the high-energy shift of this peak is due to the increase in the ligand-field splitting. As shown in Fig. 4, the intensity of the peak in normalized XANES spectra increases with an increase in the electronegativity of the bonding ligand. It is well known that the L_{III}-edge white line is sensitive to the electron density of the transition-metal compounds; the white line intensity increases with a decrease in the electron density of the Pd $4d$ level [35]. The observed increase in the peak intensity could be due to the increase in the iconicity in the Pd–X bonds, which should correspond to the decrease in the electron density of the Pd $4d$ level. For Pd–sepiolite, the peak position (3175.8 eV) is intermediate between those for $[Pd(NH_3)_4]^{2+}$ (3176 eV) and $Pd(OAc)_2$ (3175.4 eV), which suggests that the ligand-field splitting of the supported Pd(II) species is intermediate between these compounds. This interpretation

Table 1
Reactions of 4-bromophenol with sodium tetraphenylborate by various catalysts[a]



Run	Catalysts (wt%)[b]	Yield[c] (%)
1	Pd–sepiolite (0.5)	99 (99)
2	Pd–NaY (0.7)	83
3	Pd–mica (0.7)	73
4	Pd/C (2)	23
5	Pd–SiO_2 (0.5)	57
6	$PdCl_2$	47
7	$Pd(OAc)_2$	36
8	$Pd(OAc)_2$[d]	43

[a] Reaction conditions: 4-bromophenol (1.0 mmol), Ph_4BNa (0.27 mmol), Na_2CO_3 (1.5 mmol), catalyst (0.1 mol% Pd) in H_2O (10 cm^3) at room temperature for 5 h in air.

[b] Pd content of the supported catalyst.

[c] GC yield using n-nonane as an internal standard after extraction by ethyl acetate. The isolated yield is in parenthesis.

[d] Catalyst amount = 1.0 mol%.

is consistent with the UV-Vis result, suggesting the substitution of several NH_3 ligands by the oxygen of the support. For Pd–sepiolite, the intensity of the peak is higher than those for $[Pd(NH_3)_4]Cl_2$ and $Pd(OAc)_2$. This may be due to a decrease in the electron density of the Pd 4*d* level caused by a strong electrostatic interaction between anionic clay oxygen and Pd(II) cations. From these results, Pd species in Pd–sepiolite are proposed to be the Pd(II) cations immobilized on the anionic surface oxygens of the sepiolite.

For the reference compounds of the metallic Pd, Pd black was used instead of Pd foil. Note that the XRD pattern of Pd black showed that Pd black consists of highly crystallized Pd metal. From the spectrum of Pd black, it is clear that the characteristic XANES feature for the highly crystallized Pd metal is a small peak at 3174.2 eV. For Pd/C catalyst, a relatively small peak at 3175.4 eV due to oxidized Pd species and a shoulder around 3174.2 eV due to the Pd metal are observed. This result seems to be inconsistent with XRD and Pd K-edge XANES/EXAFS results of Pd/C (Figs. 2 and 3), which strongly indicate that small Pd metal particles are predominant Pd species on Pd/C. This inconsistency should be derived from a high sensitivity of the L_{III}-edge XANES to the oxidation states and may be explained as follows. The metallic Pd particles on carbon are in slightly oxidized states possibly by the influences of the support surface or the oxygen atoms on the surface of Pd metal particles.

3.2. Catalytic properties of Pd–sepiolite for Suzuki-type reactions

Table 1 list the results of the coupling reaction of 4-bromophenol and sodium tetraphenylborate. In entries 1–7, the product yields for various catalyst were compared under the same conditions (0.1 mol% Pd at room temperature in air). As reported by Sakurai et al., Pd/C was not effective for the reaction with bromophenol. Although Bumagin et al. reported that phosphine-free Pd(II) catalysts such as $Pd(OAc)_2$ were effective for Suzuki reactions in water, $Pd(OAc)_2$ showed moderate a yield (36%) under our conditions, and the yield was not markedly increased even when the catalyst amount was increased (1 mol% Pd). Clearly, Pd(II) catalysts supported on ion-exchangeable solids (Pd–sepiolite, Pd–NaY, and Pd–mica) showed higher yields than unsupported Pd(II) salts and commercially available solid palladium catalyst (Pd/C). Among these catalysts, Pd–sepiolite catalyzed the cross-coupling reaction with the highest yield. For a comparison, $[Pd(NH_3)_4]Cl_2$ impregnated to the non-ion-exchangeable support, Pd–SiO_2, was tested for the reaction. With this catalyst the yield was much lower than that achieved by Pd–sepiolite, and the color of Pd–SiO_2 changed from white to gray during the reaction. Since the surface area of amorphous silica (303 $m^2\ g^{-1}$) was higher than that of sepiolite (248 $m^2\ g^{-1}$), it is assumed that the electrostatic interaction between the Pd(II) complex and the anionic surface site of the clay is important to achieve active and stable catalysis.

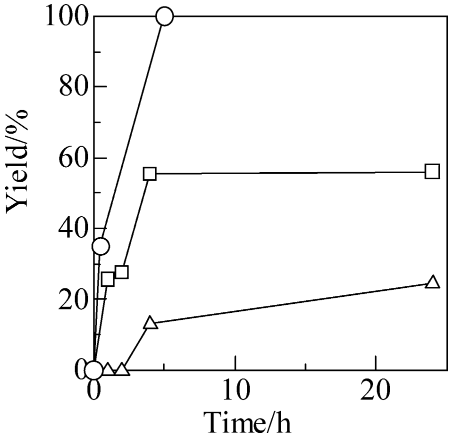


Fig. 5. Plot of yield versus reaction time for the Suzuki reaction in water at room temperature: (○) Pd–sepiolite, (□) $Pd(OAc)_2$, (△) Pd/C.

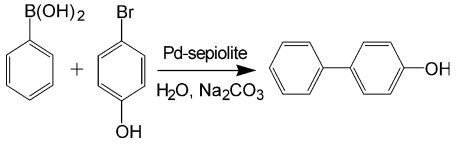
Fig. 5 compares the time course of the reaction with Pd–sepiolite, $Pd(OAc)_2$, and Pd/C. The Pd/C, consisting of the metallic Pd particles, showed the lowest reaction rate. Although $Pd(OAc)_2$ showed a comparable initial rate as Pd–sepiolite, the catalysts readily deactivated, and the formation of black Pd particles was confirmed after extraction of the products with ethyl acetate. With Pd–sepiolite, in contrast, a quantitative conversion was attained after 5 h. To confirm heterogeneity of Pd–sepiolite, we performed the leaching test for the reaction of 4-bromophenol [36]. After stirring the reaction mixture for 1 h in the presence of 0.05 mol% of Pd–sepiolite (yield = 38%) followed by filtering off the catalyst, the total Pd content in the filtrate was only 0.02 ppm. With filtrate the reaction did not further proceed after 5 h, which proves heterogeneous catalysis of Pd–sepiolite. The activity of the recovered Pd–sepiolite is shown in Table 2. After the

Table 2
Reactions using recovered Pd–sepiolite[a]

Cycles	Yield (%)
	> 99
First reuse	95
Second reuse	> 99
Third reuse	97

[a] Reaction conditions: 4-bromophenol (1.0 mmol), Ph_4BNa (0.27 mmol), Na_2CO_3 (1.5 mmol), catalyst (0.1 mol% Pd) in H_2O (10 cm^3) at room temperature for 5 h in air.

Table 3
Pd–sepiolite-catalyzed Suzuki reaction of 4-bromophenol with phenylboronic acid[a]



Run	Solvent	Yield[b] (%)
1	H_2O	90[c]
2	H_2O	99
3	H_2O[d]	> 99 (94)
4	MeOH	0
5	1,4-Dioxane	0
6	DMF	0
7	DMF/H_2O (1/1)	21

[a] Reaction conditions: 4-bromophenol (1 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (3 mmol), catalyst (0.1 mol% Pd), H_2O (10 cm^3) at room temperature in air for 20 h.

[b] GC yield using n-nonane as an internal standard after extraction by ethyl acetate. The isolated yield is in parentheses.

[c] Reaction was performed in N_2.

[d] Reaction conditions: 4-bromophenol (50 mmol), phenylboronic acid (60 mmol), Na_2CO_3 (300 mmol), catalyst (0.0001 mol% Pd), H_2O (500 cm^3) at reflux temperature in air for 24 h.

reaction, ethyl acetate was added to the reaction mixture, and the solid catalyst was removed by centrifugation, followed by washing with water to remove Na_2CO_3 and borates. The catalyst powder was reused at least 3 times without indication of the catalyst deactivation, which confirms a high stability of this catalyst. Bulut et al. tested the recycle of Pd–NaY catalyst for the Suzuki reaction in DMF/H_2O solvent and reported that the used catalyst should be recalcined under O_2 in order to regenerate its activity [17]. Hence, a simple procedure for catalyst recycle is an additional advantage of Pd–sepiolite catalyst.

Table 3 shows results of the Suzuki reaction of 4-bromophenol with phenylboronic acid under various conditions. In water as a solvent, Pd–sepiolite was effective under air as well as under an inert atmosphere; almost quantitative yields were obtained under each condition. In a serious of experiments carried out using 0.1 mol% Pd–sepiolite at room temperature in air (runs 2, 4–7), the solvent was varied. A remarkable effect of the solvent was observed. The reaction did not proceed with organic solvents such as methanol, 1,4-dioxane, and DMF at room temperature. In mixtures of DMF and H_2O, only 22% yield was obtained. To evaluate the durability of the Pd–sepiolite, we have examined the Suzuki reaction with a significantly low catalyst concentration (run 3). In the cross-coupling of 4-bromophenol with phenylboronic acid in water at reflux temperature with 0.0001 mol% of palladium, a complete conversion of 4-bromophenol and an isolated yield of 94% were obtained after 24 h, corresponding to TON value of 940,000. To the best of our knowledge, this is the highest TON for the heterogeneously catalyzed Suzuki cross-coupling of aryl bromides. However, when 4-chlorophenol was used for the reaction with phenylboronic acid by Pd–sepiolite (0.2 mol%) under reflux condition, only 31% yield was obtained, indicating that the catalyst is not applicable for the coupling reaction of aryl-chlorides.

3.3. *Structure of the catalyst after the Suzuki reaction*

During the catalytic cycle, a part of the Pd(II) complexes initially present in the catalyst can be reduced to Pd(0) intermediates via a reductive-elimination process. The Pd(0) complex should be the most unstable Pd species in the present reaction. Inactive large Pd particles are known to be formed through the aggregation of the active Pd(0) species [8]. To clarify the aggregation behavior, various spectroscopic characterizations were carried out on the Pd species formed during the Suzuki reaction. The XRD pattern of Pd–sepiolite after the reaction was essentially the same as that of the fresh sample, indicating no structural damage of the support and no formation of large Pd particles during the reaction. As shown in Fig. 2, the feature of Pd K-edge XANES for the used Pd–sepiolite is essentially the same as that of fresh sample, but it is clearly different from that of Pd/C or Pd foil. In the Pd K-edge EXAFS spectrum of the used Pd–sepiolite (Fig. 3), the peak around 0.16 nm due to Pd–O and/or Pd–N is still predominant, but a small peak at 0.25 nm due to the adjacent Pd atom is observed. These results indicate that the highly dispersed Pd(II) cations are predominant Pd species, but Pd clusters are also present as minor species on the used catalyst. The Pd L_{III}-edge XANES spectrum of the used Pd–sepiolite is shown in Fig. 4. Although the intensity of the white line peak slightly decreased after the reaction, the peak position did not change. This indicates that the oxidation state of the Pd species in the catalyst did not markedly change during the reaction. A slight decrease in the intensity should be caused by the presence of the Pd clusters. TEM images of the used Pd–sepiolite are shown in Fig. 6. Over most of the sepiolite surface, Pd particles were not observed as illustrated in Fig. 6a. However, a small number of Pd clusters (2–7 nm) were also observed on the external surface of the sepiolite (Fig. 6b). Considering the Pd K-edge and Pd L_{III}-edge XANES results that the average Pd oxidation state of the Pd–sepiolite did not markedly change after the reaction, it can be concluded that the Pd metal clusters observed in TEM images are the minor

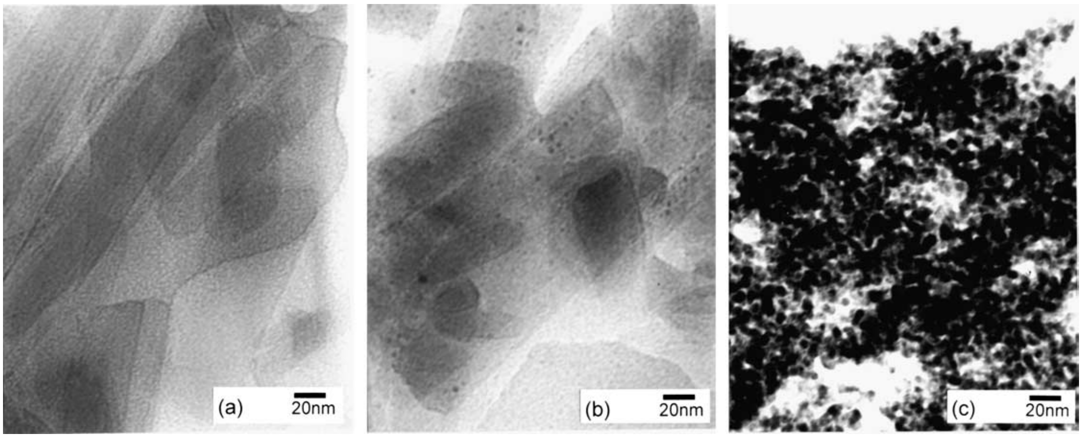


Fig. 6. TEM images of the catalysts after the Suzuki reaction: Pd–sepiolite (a, b) and Pd–SiO_2 (c).

species. The small peak due to the adjacent Pd atom shown in EXAFS is caused by the presence of such metal clusters.

When the $[Pd(NH_3)_4]^{2+}$ complex dispersed on the non-ion-exchangeable support (Pd–SiO_2) and Pd(II) complexes in the absence of the solid support were tested for the Suzuki-type reaction (Table 1), their activities were lower than that of Pd–sepiolite. In addition, the change in color suggests the Pd metal precipitation during the reaction. As shown in Fig. 2, the Pd K-edge XANES spectrum of Pd–SiO_2 significantly changed after the reaction, and its feature was close to that of Pd foil and Pd/C. TEM image of Pd–SiO_2 after the reaction (Fig. 6c) shows the presence of Pd metal particles of around 10–100 nm in size. The black powders precipitated during the reaction with $Pd(OAc)_2$ catalyst were also collected and were used for Pd K-edge XAFS measurement. The XANES and EXAFS spectra showed characteristic features for metallic Pd particles, confirming the formation of metal particles during the reaction by $Pd(OAc)_2$. In contrast, as noted, the characterization results of the used Pd–sepiolite indicate that the change in the structure of Pd species after the reaction is not significant; the highly dispersed Pd(II) complexes are still present as main Pd species together with the small Pd particles as minor species. From these results, it is concluded that the Pd metal precipitation during the reaction and resulting loss of the activity can be suppressed by the use of the sepiolite support, and this results in the high durability of Pd–sepiolite. The electrostatic interaction between the anionic surface oxygen of the sepiolite and the cationic Pd(II) precursors or Pd(II) intermediates could be effective for suppressing the leaching of Pd in the solution and the subsequent metal precipitation. Several studies showed the use of Pd metal nanoparticles as effective catalysts for coupling reactions. Reetz et al. proposed that nano-sized Pd colloids in situ generated from Pd(II) precursor during the Heck reaction act as effective heterogeneous catalysts [7]. Li et al. showed that polymer-stabilized Pd nanoparticles have high activity for Suzuki reactions [8]. However, the nanoparticles were agglomerated after one cycle, resulting in a loss of catalytic activity [8]. It is reasonable to assume that the Pd clusters observed in the recovered Pd–sepiolite are also the catalytically active species. For Pd–SiO_2 and $Pd(OAc)_2$ catalysts tested in this study, it is speculated that nano-sized Pd colloids generated during the Suzuki reaction act as catalytically active species, though such nanoparticles should be further agglomerated to inactive large metal particles as characterized by Pd K-edge XAFS and TEM.

4. Conclusion

$[Pd(NH_3)_4]^{2+}$-exchanged sepiolite clay (Pd–sepiolite) was shown to be highly active for the catalytic Suzuki-type carbon–carbon coupling reactions of 4-bromophenol with phenylboronic acid or sodium tetraphenylborate in water. The Pd(II) complexes exchanged to the sepiolite were present as the main Pd species in Pd–sepiolite even after the reaction, accompanying the formation of 2–7 nm Pd clusters as minor species, indicating that Pd sites are highly dispersed even under the reaction conditions. Although the unsupported Pd(II) salt showed a comparable initial rate as Pd–sepiolite, it readily deactivated by forming inactive Pd metal particles. Owing to the high structural stability, Pd–sepiolite showed a significantly high turnover numbers ($TON = 940{,}000$) under a reflux condition, and it showed a good recyclability. This novel catalyst provides a clean and convenient alternative for Suzuki reaction in view of the following advantages. The reaction proceeds smoothly at room temperature in water media without the need to use organic solvents, degassing of solvent, and inert atmosphere. The catalyst is also stable, easy to handle, reusable, and nonpolluting solid.

Acknowledgment

The X-ray absorption experiments were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2003G-274).

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