# A Convoluted Polymeric Imidazole Palladium Catalyst: Structural Elucidation and Investigation of the Driving Force for the Efficient Mizoroki–Heck Reaction

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MPPI-Pd (7 mol ppm Pd), prepared from poly(*N*-isopropylacrylamide-*co-N*-vinylimidazole) and  $(NH_4)_2PdCl_4$  by our molecular convolution method, promoted the Mizoroki–Heck reaction in water to give the corresponding coupling products with high yield and reusability. To clarify why the catalyst was so active, structural elucidation and temperature-dependent absorption/discharge investigation were performed using X-ray absorption fine structure analysis, Raman and far-IR spectroscopy, elemental analysis, and DFT calculations, which provided

#### Introduction

The development of highly active and reusable polymer-supported metal catalysts is an important topic for synthetic organic chemistry, green chemistry, and medicinal chemistry as well as for chemical and pharmaceutical processes.<sup>[1]</sup> These catalysts can be applied to the chemical preparation of pharmaceutical compounds, electrofunctional materials, and organic electroluminescent materials without contamination of metal species. We have developed a highly active and reusable convoluted polymeric palladium catalyst (MPPI-Pd, 3) from poly(Nisopropylacrylamide-co-N-vinylimidazole) (1) and (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> (2) (Scheme 1), which was applied to the allylic arylation and the Suzuki-Miyaura reaction in water.<sup>[2]</sup> The catalyst with 0.28-66 mol ppm Pd (0.000028-0.0066 mol % Pd) promoted allylic arylation and the Suzuki-Miyaura reaction with high recyclability. To clarify why MPPI-Pd has a high catalytic activity, it is important to investigate the structure of the Pd complex and the mechanism of the absorption/discharge of organic substrates (aryl halides, etc.) and water in MPPI-Pd.

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the structure of cis-PdCl<sub>2</sub>L<sub>2</sub> (L=imidazole moiety). Moreover, the temperature-dependent absorption and discharge of aryl iodides and water in MPPI-Pd were observed with near-IR spectroscopy and macroscopic observations. The efficient diffusion of organic substrates into the internal nanospaces in MPPI-Pd and the following discharge of the water molecules at 80 °C should enhance the catalytic activity dramatically as the driving force of the reaction.



Scheme 1. Preparation of MPPI-Pd.

The structural elucidation of insoluble and amorphous polymeric metal catalysts is quite difficult because XRD, mass analysis, and other analytical methods to characterize homogeneous catalysts are generally not useful because of the polymeric nature of the catalysts. X-ray absorption fine structure (XAFS) spectroscopy could be a powerful method to determine these structures.<sup>[3]</sup> Although the determination of inorganic<sup>[4]</sup> and homogeneous<sup>[5,6]</sup> catalysts as well as metal-containing biomolecules<sup>[7]</sup> has been shown, the structural elucidation of polymeric metal catalysts using XAFS is still evolving and challenging.<sup>[8]</sup>

Here, we found that MPPI-Pd [7 mol ppm Pd (0.0007 mol % Pd)] promoted the Mizoroki–Heck reaction efficiently in water to give the corresponding coupling products with high yield and reusability without hydrolysis of the products. We report the structural elucidation of MPPI-Pd using X-ray absorption near-edge structure analysis (XANES), extended X-ray absorption fine structure analysis (EXAFS), Raman and far-IR (FIR) spectroscopy, and DFT calculations. Moreover, the tempera-



ture-dependent absorption and discharge of aryl iodides and water in MPPI-Pd was investigated by utilizing near-IR (NIR) spectroscopy and macroscopic observations to show the dynamic mechanism that enhances the catalytic activity.

#### **Results and Discussion**

#### MPPI-Pd-catalyzed Mizoroki-Heck reaction

Here, MPPI-Pd was utilized to catalyze the Mizoroki–Heck reaction in water to show its high catalytic activity and generality. It is an important challenge to develop highly active and reusable polymeric metal catalysts as this coupling is a useful reaction in synthetic organic chemistry to supply pharmaceutical, agricultural, and functional materials.<sup>[9,10,11,12]</sup> In particular, since Buchmeiser and Wurst reported a highly active polymer-supported Pd catalyst for the Mizoroki–Heck reaction,<sup>[12]]</sup> the development of highly active and reusable polymer-supported Pd catalysts has been watched with interest. Moreover, the Mizoroki–Heck reaction of alkyl acrylates in water is challenging because hydrolysis is a fatal side reaction.

The reusability of MPPI-Pd was investigated in the Mizoroki– Heck reaction of iodobenzene (**4a**) and butyl acrylate (**5a**) with triethylamine and tetrabutylammonium bromide (TBAB) at 100 °C for 17 h in water without the use of organic solvents, which affords butyl cinnamate (**6a**) in 99% yield (Table 1). The

Table 1. Reusability of MPPI-Pd in the in-water Mizoroki–Heck reaction of 4a and 5a. <sup>[a]</sup> Yields given in %.				
First use	Second use	Third use	Fourth use	Fifth use
99	98	97	95	96
[a] Conditions: <b>4a</b> (1 mmol), <b>5a</b> (2 mmol), <b>3</b> (330 nmol Pd, 0.5 mg), Et <sub>3</sub> N (3 mmol), TBAB (0.20 mmol), water (1.5 mL), 100 °C, 17 h.				

reused catalyst promoted the reaction efficiently to give **6a** in 98, 97, 95, and 96% yield in the second to fifth consecutive runs. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) indicated that Pd was not present in the reaction mixture. This result as well as our previous studies, which include the hot leaching test,<sup>[2]</sup> indicate that MPPI-Pd works as a heterogeneous catalyst.

The in-water Mizoroki–Heck reaction of various aryl iodides **4** and olefins **5** was performed with 7 mol ppm Pd (0.0007 mol% Pd; Table 2). The reaction of electron-deficient substrates **4b–d** proceeded smoothly to give the corresponding butyl cinnamates **6b–d** in 96–99% yield with a turnover number (TON) of approximately 140000 (Entries 2–4). Electronrich materials **4e–f** were converted readily to the corresponding coupling products **6e–f** in 95 and 99% yield under similar conditions (Entries 5–6). The reaction of a substrate that bears a pyridine ring **4g** afforded the product **6g** in 94% yield (Entry 7). The coupling with styrene (**5b**) was also performed in water under similar conditions to give the corresponding stilbenes in 93–96% yield (Entries 9–13). *N*-Isopropylacrylamide

Table 2. Mizoroki–Heck reaction with 7 mol ppm Pd of 3. <sup>[a]</sup>				
	R <sup>1</sup> -I * >> R <sup>2</sup> 4 5	MPPI-Pd (7 mol ppm Pd) (0.0007 mol % Pd) EtsN (3 mol equiv) TBAB (20 mol %) H2O, 100 °C, 17 h	► R <sup>1</sup> ~ R <sup>2</sup> 6	
Entry	R <sup>1</sup> <b>4</b>	R <sup>2</sup> 5	Product 6	Yield [%]
1	Ph <b>4a</b>	CO <sub>2</sub> Bu <b>5 a</b>	ба	96
2	4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> <b>4 b</b>	5 a	6 b	99
3	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> 4 c	5 a	бc	96
4	4-AcC <sub>6</sub> H <sub>4</sub> <b>4 d</b>	5 a	6 d	96
5	4-MeC <sub>6</sub> H <sub>4</sub> <b>4 e</b>	5 a	бe	95
6	4-MeOC <sub>6</sub> H <sub>4</sub> <b>4 f</b>	5 a	6 f	99
7	3-pyridyl <b>4g</b>	5 a	6 g	94
8 <sup>b</sup>	1-naphthyl <b>4 h</b>	5 a	6 h	96
9	4a	Ph <b>5 b</b>	6i	96
10	4 b	5 b	6j	94
11	4-NCC <sub>6</sub> H <sub>4</sub> <b>4i</b>	5 b	6 k	96
12	4e	5 b	61	93
13	4 f	5 b	6 m	95
14	4a	CONH- <i>i</i> Pr <b>5 c</b>	бn	96
15	4e	5 c	60	94
16	4 f	5 c	6 p	95
[a] Conditions: <b>4</b> (1 mmol), <b>5</b> (2 mmol), <b>3</b> (7 nmol Pd; 0.01 mg), $Et_3N$ (3 mmol), TBAB (0.20 mmol), $H_2O$ (1.5 mL), 100 °C, 17 h; [b] <b>3</b> (20 nmol Pd), 48 h.				

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(5 c) was a suitable reagent for the reaction and gave the corresponding  $\alpha$ , $\beta$ -unsaturated amides **6 n**-**p** in 94–96% yield (Entries 14–16).

MPPI-Pd was applied to the more challenging Mizoroki– Heck reaction of the less reactive substrate aryl bromide and chloride without the use of organic solvents (Scheme 2). When



Scheme 2. Mizoroki–Heck reaction of aryl bromide and chloride.

the reaction of bromobenzene (7) and **5a** was performed with 66 mol ppm Pd (0.0066 mol%) of MPPI-Pd in the presence of NaOAc and TBAB at 140 °C for 20 h, we were pleased to find that the reaction proceeded smoothly to give **6a** in 82% yield. The reaction of 4'-chloroacetophenone (**8**) and **5a** was performed under similar conditions to afford the coupling product **6d** in 85% yield.

#### Structural elucidation of MPPI-Pd

It is important but difficult to clarify the structure of MPPI-Pd to consider its high catalytic activity. First, the coordination structure of MPPI-Pd was investigated to examine the structure of the Pd complex. The Pd K-edge XANES spectrum of MPPI-Pd



Figure 1. First derivative XANES spectra of MPPI-Pd and some reference compounds  $[(NH_4)_2PdCl_2$  and PdCl\_2 for Pd^I; Pd(PPh\_3)\_4 and Pd black for Pd^0].

was compared with that of Pd<sup>II</sup> species ((NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> and PdCl<sub>2</sub>) and Pd<sup>0</sup> species (Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd black). The first derivative of the XANES spectrum of MPPI-Pd was more similar to the reference compounds for Pd<sup>II</sup> than those of Pd<sup>0</sup> (Figure 1). This result suggested strongly that the oxidation state and the coordination geometry of the Pd center in MPPI-Pd was squareplanar Pd<sup>II</sup>. Although Pd<sup>0</sup> species were also detected in MPPI-Pd,<sup>[2]</sup> this result suggested that the major species in MPPI-Pd is Pd<sup>II</sup>. Elemental analysis of MPPI-Pd (Supporting Information) implied that two CI atoms and possibly two N atoms coordinate to the Pd center. The Raman spectrum showed a broad peak near  $\tilde{\nu} =$ 290 cm<sup>-1</sup>, and two peaks were revealed at  $\tilde{v} = 287/295 \text{ cm}^{-1}$  in the second derivative spectrum (Figure 2a and b). The set of split peaks in the latter spectrum correspond to the symmetric/ asymmetric CI-Pd-CI stretching CHEMCATCHEM Full Papers

vibrations in *cis*-Pd<sup>II</sup>Cl<sub>2</sub>L<sub>2</sub>.<sup>[13,14]</sup> The FIR spectrum supported these observations (Figure 2 c and d). Based on these results, *cis*-PdCl<sub>2</sub>L<sub>2</sub> (L=imidazole moiety of the polymeric ligand) was the most likely local structure. Therefore, the structure of *cis*-PdCl<sub>2</sub>(1-methylimidazole)<sub>2</sub> was optimized by DFT calculation at the level of B3LYP/def2-TZVP (Figure 3).<sup>[15]</sup> The fitting analysis of the Pd K-edge Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectrum of MPPI-Pd was performed using the DFT model (Figure 4). The best fitting result was obtained for the parameters given in Table 3. The scattering paths of Pd–Cl, Pd–N (3-N in 1-methylimidazole), and Pd–C (likewise 2-C and 4-C) were included in the fitting *R* range. The good agreement of the experimental data of FT-EXAFS with the DFT model was consistent with the results of vibrational spectroscopy. These results suggested that the co-

<b>Table 3.</b> Fitted parameter values of FT-EXAFS with the DFT model of $PdCl_2(1-methylimidazole)_2$ . <sup>[a]</sup>						
R-range	<i>k</i> -range	R factor	$\Delta E$	$\Delta R(CI)$		
1.2–2.9 Å	3–15 Å <sup>–1</sup>	0.012	+2.85 eV	+0.01 Å		
$\Delta R(N)$	$\Delta R(C)$	$\sigma^2(CI)$	σ²(N)	σ²(C)		
−0.07 Å	−0.10 Å	0.004 Å <sup>2</sup>	0.005 Å <sup>2</sup>	0.003 Ų		
[a] The coordination number of Pd was fixed by the model structure.						



Figure 2. Low-frequency Raman and FIR spectra of MPPI-Pd: a) Raman spectrum, b) second derivative of Raman spectrum, c) FIR spectrum, and d) second derivative of FIR spectrum. Black arrows indicate split Pd–Cl stretching vibrations.

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**Figure 3.** DFT-optimized geometry of the model structure, *cis*-PdCl<sub>2</sub>(1-meth-ylimidazole)<sub>2</sub>, for MPPI-Pd at the level of B3LYP/def2-TZVP. For simplicity, the polymer ligands **1** were substituted for 1-methylimidazole (green: Pd, yellow: Cl, blue: N, gray: C, white: H). Selected internuclear distances: Pd-Cl=2.31 Å, Pd-N=2.08 Å.



**Figure 4.**  $k^3$ -Weighted FT-EXAFS of MPPI-Pd (solid line) and the best fit with the DFT-optimized geometry of *cis*-PdCl<sub>2</sub>(1-methylimidazole)<sub>2</sub> (dashed line).

ordination structure of the Pd center in MPPI-Pd was *cis*-PdCl<sub>2</sub>L<sub>2</sub> (L = imidazole moiety in the polymeric ligand 1). Moreover, a comparison of the NIR spectra of MPPI-Pd and 1 indicated clearly that almost all of the imidazole moieties in MPPI-Pd contributed to the coordination to the Pd atoms because the overtones of the C–H stretching vibrations derived from imidazoles were shifted significantly to higher wavenumbers after complexation with Pd<sup>2+</sup> (Figure 5).

#### Temperature-dependent absorption and discharge

Not only the elucidation of the local structure near the Pd complex but also the analysis of the thermally dependent dynamic structure of MPPI-Pd is important to find the reason for its high catalytic activity. During the catalytic reaction, we observed the temperature-dependent high absorption/discharge ability for organic molecules and water at 23 and 80 °C.

Thus, a disk of MPPI-Pd (30 mg,  $\varnothing$  10 mm, prepared by using a  $\varnothing$ 10 mm mold at 20 MPa for 10 min under vacuum at 23 °C) repelled water at 80 °C, whereas at 23 °C it swelled in water (Figure 6). Notably, MPPI-Pd deformed in water at 80 °C, and its surface was apparently dry. This is probably because 1, a polymeric component of MPPI-Pd, shows a lower critical solution temperature (LCST) phase transition<sup>[16]</sup> at 35 °C (the poly-



**Figure 5.** NIR spectra of MPPI-Pd (top left) and 1 (bottom left) in the range of  $\tilde{\nu}$  = 6400–6000 cm<sup>-1</sup>. Overtones of C–H stretching vibrations (denoted as b and c, see also Figure 7) of imidazole moiety in 1 (center) and MPPI-Pd (right). Imidazoles are shown in red.

mer 1 was soluble/insoluble in water below/over 35 °C). Waterswollen MPPI-Pd shrank in water if it was heated gradually from 23 to 80 °C, whereas it swelled more if it was cooled from 23 to 5 °C (Figure S3). In contrast, MPPI-Pd absorbed **4a** at 80 °C to swell to 1.4 times larger in diameter, whereas it absorbed **4a** but did not swell at 23 °C.

As we believe that the dynamic phenomena of the temperature-dependent absorption and discharge pathway is one of the driving forces that promotes efficient reaction, we investigated MPPI-Pd in water and 1-iodonaphthalene  $(4 h)^{[17]}$  at 23 and 80 °C by NIR spectroscopy.

NIR spectroscopy is one of the most powerful methods to survey the changes in the intermolecular interaction and the microenvironment of insoluble polymer catalysts through the overtone and combination bands derived from X–H (X=C, N, O, etc.) vibrations because of the high transmittance of NIR light and sufficient spectral resolution compared with middle-IR (MIR) spectroscopy.<sup>[18]</sup> The NIR experiment was performed using the above-mentioned 10 mm disks of solid samples.

The NIR spectra of MPPI-Pd and 1 and their assignment in the range of  $\tilde{\nu} = 4000-7000 \text{ cm}^{-1}$  are shown in Figure 7. The spectra of both MPPI-Pd and 1 were quite similar to that of poly(N-isopropylacrylamide) (PNIPAM) except for the absorption bands in the range of  $\tilde{\nu} = 6000-6300$  and 5000-5300 cm<sup>-1</sup>. As the overtone and combination bands of PNIPAM in the NIR region have been fully characterized by Wu et al.,[19] we followed their assignment in relation to the absorption bands derived from the PNIPAM-like structure in 1 and assigned the absorption bands around  $\tilde{\nu} = 6000 - 6300 \text{ cm}^{-1}$  exclusively to the overtone of the C-H stretching vibration of imidazoles in MPPI-Pd and 1 (Figures 5 and 7, bands b and c). The prominent absorption bands in the range of  $\tilde{\nu} = 5000-5300 \text{ cm}^{-1}$  were attributed to the combination of bending and symmetric/asymmetric stretching of water in the polymer matrix (Figure 7, band a).

The  $\emptyset$ 10 mm disk of MPPI-Pd was heated and cooled under aerobic conditions that included moisture to observe the absorption and discharge of water to/from MPPI-Pd. First, MPPI-





Figure 6. Morphology of MPPI-Pd in water and  $4\,a$  at 23 and 80  $^\circ\text{C}$  from 0 to 4 h.

Pd was heated at 80 °C for 30 min and then allowed to cool at 23 °C. The sample was continuously exposed to air over 6 h at 23 °C and 35% relative humidity. During the process, reversible changes in the NIR spectra were observed (Figure 8). Thus, the heating of as-prepared MPPI-Pd at 80 °C provided a decreased absorbance of water ( $\tilde{\nu} = 5000-5300 \text{ cm}^{-1}$ ) and a change in the intensity of the combination bands in the range of  $\tilde{\nu} = 4000-4200 \text{ cm}^{-1}$  ([ $v_{as}$ (CH<sub>3</sub>)+CH<sub>2</sub> rocking], [ $v_{as}$ (CH<sub>3</sub>)+CH<sub>3</sub> rocking], and [ $v_{as}$ (CH<sub>3</sub>)+CH<sub>3</sub> skeletal]). The changes were restored within 6 h at 23 °C in air. A similar result was also obtained for **1** (Figure S4). These results indicated that both MPPI-Pd and **1** desorbed water molecules at an elevated temperature (80 °C)



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**Figure 7.** NIR spectra of MPPI-Pd and 1. Selected peak assignment: a)  $2 \times v(NH)_{f_{7}}$  b, c)  $2 \times v(CH)_{imidazole}$ ; d)  $2 \times v_{\alpha\sigma}(CH_{3})$ ; e)  $2 \times v_{\alpha\sigma}(CH_{2})$ ; f)  $2 \times v_{\sigma}(CH_{3})$ ; g)  $v_{\sigma/\alpha\sigma}(OH)_{water} + \delta(OH)_{water}$ ; h)  $v(NH)_{b}$ +Amide II; i) Amide B+Amide II; j)  $v(NH)_{b}$ +Amide III; k)  $v_{as}(CH_{3}) + \delta_{as}(CH_{3})$ ; l)  $v_{s}(CH_{3}) + \delta_{as}(CH_{3})$ ; m)  $v_{as}(CH_{3}) + CH_{3}$ skeletal; n)  $v_{as}(CH_{3}) + CH_{3}$  rocking; o)  $v_{as}(CH_{3}) + CH_{2}$  rocking.



**Figure 8.** Heating and cooling of MPPI-Pd to see the adsorption and desorption of water; a) as-prepared MPPI-Pd, b) heated at 80 °C for 30 min, c) after 30 min at 23 °C, d) after 2 h at 23 °C, e) after 6 h at 23 °C.

adsorbed water from the air at 23 °C reversibly. Notably, the  $[2 \times \nu(CH)_{imidazole}]$  band of MPPI-Pd did not significantly change during the heating and cooling process (Figure 5). Consequently, the local structure of the Pd-imidazole complex in MPPI-Pd was thermally stable.

The heating and cooling experiment was examined in the presence of **4h**. When MPPI-Pd was heated at 80 °C for 30 min, and **4h** ( $\approx 2 \,\mu$ L) was placed directly on the disk of MPPI-Pd at 80 °C, **4h** soaked into it readily, and further changes in the relative intensity of the combination bands ( $\tilde{\nu} = 4000-4200 \,\mathrm{cm^{-1}}$ ) were observed (Figure 9).<sup>[20]</sup> The changes were restored within 6 h at 23 °C. In contrast, when **4h** was added to as-prepared MPPI-Pd at 23 °C, no significant spectral change was observed in terms of the water ( $\tilde{\nu} = 5000-5300 \,\mathrm{cm^{-1}}$ ) and combination bands ( $\tilde{\nu} = 4000-4200 \,\mathrm{cm^{-1}}$ ; Figure S5).

Meanwhile, small wavenumber shifts of overtone bands of the C–H asymmetric stretching of CH<sub>3</sub> and CH<sub>2</sub> ([2× $\nu_{as}$ (CH<sub>3</sub>)], [2× $\nu_{as}$ (CH<sub>2</sub>)]) in the range of  $\tilde{\nu}$  = 5800–6000 cm<sup>-1</sup>, in which CH<sub>3</sub> derived from the *N*-isopropyl group and CH<sub>2</sub> derived from the main chain of the polymer, were also observed. The wavenum-



**Figure 9.** Heating and cooling of MPPI-Pd with the addition of 1-iodonaphthalene (**4**h, 1-INaph) at 80 °C; a) as-prepared MPPI-Pd, b) heated at 80 °C for 30 min, c) 1-iodonaphthalene was added at 80 °C, d) after 30 min at 23 °C, e) after 2 h at 23 °C, f) after 6 h at 23 °C.

bers of the  $[2 \times v_{as}(CH_3)]$  (x axis) and  $[2 \times v_{as}(CH_2)]$  bands (y axis) of MPPI-Pd under various conditions are summarized in Figure 10. If MPPI-Pd was heated and cooled between 23 and 80 °C in air (as shown in Figure 8), water was desorbed and readsorbed, and the  $[2 \times v_{as}(CH_2)]$  and  $[2 \times v_{as}(CH_3)]$  bands changed reversibly (Figure 10, from (a) to (e), blue arrows). However, the addition of **4h** to MPPI-Pd at 80 °C (as shown in Figure 9) led to different changes in the  $[2 \times v_{as}(CH_3)]$  and  $[2 \times v_{as}(CH_2)]$  bands (Figure 10, from (b) to (f), red arrows). The re-



**Figure 10.** Plot of  $[2 \times v_{as}(CH_2)]$  versus  $[2 \times v_{as}(CH_3)]$ ; a) as-prepared MPPI-Pd, b) heated at 80 °C for 30 min, c) cooled at 23 °C after 30 min, d) after 2 h, e) after 6 h, f) 1-iodonaph-thalene added after heating at 80 °C for 30 min, g) cooled at 23 °C after 30 min, h) after 2 h, i) after 6 h, j) 1-iodonaphthalene added at 23 °C without preheating.

sulting composite was left at 23 °C in air, and further wavenumber shifts were observed (Figure 10, from (f) to (i)). Finally, the bands of  $[2 \times v_{as}(CH_2)]$  and  $[2 \times v_{as}(CH_3)]$  after 6 h (Figure 10, (i)) almost corresponded with that of the composite at 23 °C (Figure 10, (j)).

The key results are: (1) When MPPI-Pd was heated/cooled to 80/23 °C, the bands of  $[2 \times v_{as}(CH_2)]$  and  $[2 \times v_{as}(CH_3)]$  shifted reversibly. The results indicate that water was desorbed/adsorbed reversibly at a high/low temperature. This corresponds to the morphology of MPPI-Pd in water at 80/23 °C. (2) When **4h** was added to MPPI-Pd at 80 °C, the intensity of the combination bands of CH<sub>2</sub> and CH<sub>3</sub> ( $\tilde{\nu}$  = 4000–4200 cm<sup>-1</sup>) changed clearly (Figure 9). In contrast, when **4h** was added to MPPI-Pd at 23 °C, no significant spectral change was observed. These results suggested that organic substrates and reagents diffused preferably into the polymer matrix at 80 °C rather than 23 °C. This also corresponds to the morphology of MPPI-Pd in iodobenzene at 80/23 °C.

From these results as well as the observation in Figure 6, we propose and summarize a plausible mechanism of the temperature-dependent absorption/discharge of water and hydrophobic organic molecules (Figure 11). As the changes of the  $[2 \times v_{as}(CH_3)]$  and  $[2 \times v_{as}(CH_2)]$  bands were reversible and as the polymer component in MPPI-Pd comprises both a hydrophobic main chain and amphiphilic amide moieties (represented by CH<sub>2</sub> and CH<sub>3</sub>, respectively), it is proposed that MPPI-Pd has two distinct domains: a chain domain and a nanospace domain, in which the hydrophobic organic molecules (substrates and re-

> actants) and water can be absorbed. Water is absorbed in MPPI-Pd at 23 °C and is discharged at 80 °C because of the properties of the polymer 1, which has a LCST at 35 °C. When substrates and reactants are introduced at 80 °C, they are absorbed well especially in the nanospace domain in which water has been expelled. In contrast, when they are added at 23 °C, they are less absorbed, and water still exists in the nanospace domain in MPPI-Pd. If we take into account the aspects mentioned above, the efficient diffusion of organic substrates into the internal nanospaces in MPPI-Pd, which were generated by the packing of water surrounded by hydrated NIPAM units at 23 °C and the following discharge of the water at 80 °C, would enhance the catalytic activities dramatically as the driving force of the reaction. Meanwhile, the framework structure of MPPI-Pd derived from the molecular convolution of polymer chains with Pd<sup>2+</sup> helps to maintain the thermally dependent structure based on hydrogen bonding between the NIPAM units and water.

> Furthermore, as water was discharged at  $80^{\circ}$ C from MPPI-Pd and hydrophobic organic molecules were absorbed in MPPI-Pd, this phenomenon should help the Mizoroki–Heck reaction with **5a** in water. Thus, the Mizoroki–Heck reaction with **5a** should proceed smoothly without the hydrolysis of **5a** to afford the corresponding cinnamic acid esters in high yield without the formation of free cinnamic acids.



Figure 11. Plausible mechanism of temperature-dependent absorption/discharge of water and hydrophobic organic molecules.

### Conclusions

We elucidated the coordination structure of a highly active and reusable polymeric palladium catalyst MPPI-Pd, prepared poly(*N*-isopropylacrylamide-*co*-*N*-vinylimidazole) from and (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> by our molecular convolution method, which provided the coordination structure of *cis*-PdCl<sub>2</sub>L<sub>2</sub> (L=imidazole moiety of the polymeric ligand). The Mizoroki-Heck reaction proceeded with 7 mol ppm Pd (0.0007 mol % Pd) of MPPI-Pd in water to give the corresponding coupling products in >93% yield with a turnover number of approximately 140 000. Moreover, temperature-dependent absorption and discharge of aryl iodides and water in MPPI-Pd were observed by near-IR spectroscopy and macroscopic observations to investigate the reason why MPPI-Pd has high catalytic activity. We believe the elucidation and investigation of the catalytic structure and driving force for the organic transformation will help to create more highly active polymeric metal catalysts.

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