Experimental Section

Synthesis of FDU-type mesoporous polymers. Following the procedures reported previously (Zhang, F.; Meng, Y.; Gu, D.; Yan, Y.; Yu, C.; Tu, B.; Zhao, D. J. Am. Chem. Soc. 2005, 127, 13508. (b) Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Yang, H.; Li, Z.; Yu, C.; Tu, B.; Zhao, D. Angew. Chem. Int. Ed. 2005, 44, 7053), phenol (28.0 g) and aqueous solution of formaldehyde (71.0 g, 38 wt%) were added to 690.0 or 728.0 g of NaOH solution (0.1 M) and stirred at 72 °C for 1.5 h. The mixture was then cooled to room temperature and mixed well with a clear solution containing 67.2 g of Pluronic P123 (EO20PO70EO20, MW = 5800) and deionized water (700.0 g). It was then stirred continuously at 64 °C for 120 h and at 72 °C for 48 h in turn. The products of brown powders were collected by filtration and dried at 80 °C in air. After the removal of surfactant template by thermal decomposition under vacuum at 350 °C for 6 h, the mesoporous polymers of FDU-14 (Ia3d) and FDU-15 (P6mm) were obtained.

Preparation of FDU-Pd. The FDU-type mesopolymer (3.0 g) and chloromethyl methyl ether (20 mL) were first mixed and stirred at room temperature for 6 h by using anhydrous ZnCl₂ (0.9 g) as a catalyst. The chloromethylated samples, denoted as FDU-14-CH₂Cl and FDU-15-CH₂Cl, were washed repeatedly with distilled water and acetone to remove the physisorbed organic species, and finally dried in air. A subsequent amination was carried out by adding FDU-CH₂Cl (1 g) to ethylenediamine (ED) (10 g), followed by stirring at 60 °C for 6 h. The aminated products, FDU-14-ED and FDU-15-ED, were washed repeatedly with distilled water and ethanol for the purpose of removing physisorbed diamine, and finally dried in air. A subsequent reduction of Pd (II) to Pd (0) was carried out in an excess of NaBH₄ (0.1 M) to obtain mesopolymer supported Pd nanoparticles, FDU-14-Pd and FDU-15-Pd, respectively.

Characterization Methods. The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation (λ=1.5418 Å). Nitrogen adsorption-desorption isotherms were recorded at 77 K on a Quancachrome
Autosorb-3B instrument after activating the sample at 373 K under vacuum for at least 10 h. The SEM images were taken on a Hitachi S-4800 microscope, while EDS spectra was obtained on an EMAX. The TEM images were taken on a JEOL-JEM-2010 microscope. FT-IR spectra were recorded at room temperature on a Nicolet Fourier transform infrared spectrometer (NEXUS 670) using KBr technique. The wafers were evacuated at 373 K before IR spectra recording. The amount of chlorine was quantified by Volhard titration (Haouet, M.; Altissimi, M.; Framboas, M.; Galarini, R. *Accred. Qual. Assur.* **2006**, *11*, 23). The amount of nitrogen was determined by elemental analyses on a Perkin-Elmer series II 2400 CHNS analyzer. The amount of Pd was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

**Heck reaction.** Aryl halides (ArX, 10 mmol), ethyl acrylate (12 mmol), and triethylamine (NEt₃) (12 mmol) were added to 10 mL of dimethylformamide (DMF). The FDU-Pd catalyst (0.028 mol%) was added to above mixture and stirred in air. When 4-NO₂-PhBr (10 mmol) was used, the FDU-Pd catalyst was increased to 0.28 mol%. In case of Heck reaction of PhBr, PhBr (10 mmol), ethyl acrylate (12 mmol), and K₂CO₃ (12 mmol) were added to 10 mL of DMF. Then, the FDU-Pd catalyst (0.6 mol%) was added to above mixture and stirred at 140 °C for 50 h in air. The products were analyzed by GC (Shimadu 14B, FID detector, equipped with a 30-m OV-1 capillary column) using pentadecane as an internal standard. After each reaction, the used catalyst was recovered by washing with water and DMF.

**Hydrogenation reaction.** FDU-Pd (0.01g, 0.056 mol%) was suspended in methanol (50 mL). After bubbled with H₂ flow of an atmospheric pressure at 30 °C for 30 min, allyl alcohol (10 mmol) was added to the mixture to initiate the reaction. After the reaction for 30 min, the products were analyzed by GC using toluene as an internal standard.
Figure S1 Photographs illustrating the immobilization of Pd (II) ions on diamine-functionalized FDU mesopolymers.

Diamine-functionalized FDU mesopolymers sucked effectively the Pd (II) ions from yellow H₂PdCl₄ solution, which led to a colorless filtrate after filtering off the solid (above). However, the color of the filtrate was essentially the same as the H₂PdCl₄ solution in the case of unfunctionalized FDU mesopolymers (down).

Figure S2 EDS spectra of a) FDU-14,15, b) FDU-CH₂Cl, c) FDU-ED, d) FDU-Pd.

Energy Dispersive X-ray Spectrum (EDS) analysis. Compared with the parent FDU mesopolymer, FDU-CH₂Cl exhibited in EDS spectrum the characteristic peak of elementary chlorine, indicating that the CH₂Cl groups have been successfully introduced into the mesopolymer. The diamine-functionalized sample exhibited the characteristic peak of elementary nitrogen instead of Cl, indicating that amino groups have been introduced into the mesopolymer through replacing the chlorine groups in amination process. The Pd (II) ions were strongly complexed with the diamino groups, which developed the peak due to palladium.
Characterization with N\textsubscript{2} adsorption: The N\textsubscript{2} adsorption-desorption isotherms and the corresponding pore size distributions of parent FDU-type mesoporous polymers and modified samples are shown in Figure S5. All samples exhibited a typical IV type isotherm and a clear hysteresis loop at P/P\textsubscript{0} region of 0.4-0.6, characteristic of ordered mesostructures. All the pore size distributions exhibited sharp peaks due to uniformly sized pores. Compared with the parent samples, the modified samples showed a decrease in N\textsubscript{2} uptake as a result of incorporation of the organic groups or Pd particles into the channels, which was consistent with the slight narrowing in pore diameters. Moreover, the adsorption and desorption branches did not close completely at low relative pressure, due to a typical nature of these mesopolymers.\textsuperscript{1} Some typical textural parameters are listed in Table S1.

Table S1 Textural properties of FDU materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>N amount mmol/g\textsuperscript{-1}</th>
<th>Cl amount mmol/g\textsuperscript{-1}</th>
<th>S\textsubscript{BET} / m\textsuperscript{2}g\textsuperscript{-1}</th>
<th>V\textsubscript{p} / cm\textsuperscript{3}g\textsuperscript{-1}</th>
<th>D\textsubscript{p} / nm, BJH</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDU-14</td>
<td>-</td>
<td>-</td>
<td>514</td>
<td>0.42</td>
<td>3.3</td>
</tr>
<tr>
<td>FDU-14-CH\textsubscript{2}Cl</td>
<td>-</td>
<td>1.9</td>
<td>468</td>
<td>0.38</td>
<td>3.3</td>
</tr>
<tr>
<td>FDU-14-ED</td>
<td>3.6</td>
<td>-</td>
<td>364</td>
<td>0.30</td>
<td>3.0</td>
</tr>
<tr>
<td>FDU-14-Pd</td>
<td>-</td>
<td>-</td>
<td>330</td>
<td>0.26</td>
<td>2.9</td>
</tr>
<tr>
<td>FDU-15</td>
<td>-</td>
<td>-</td>
<td>439</td>
<td>0.36</td>
<td>3.6</td>
</tr>
<tr>
<td>FDU-15-CH\textsubscript{2}Cl</td>
<td>-</td>
<td>2.2</td>
<td>398</td>
<td>0.33</td>
<td>3.5</td>
</tr>
<tr>
<td>FDU-15-ED</td>
<td>4.0</td>
<td>-</td>
<td>342</td>
<td>0.29</td>
<td>3.2</td>
</tr>
<tr>
<td>FDU-15-Pd</td>
<td>-</td>
<td>-</td>
<td>312</td>
<td>0.24</td>
<td>3.0</td>
</tr>
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</table>
Figure S3  N₂ adsorption-desorption isotherms of A) FDU-14 and B) FDU-15 mesoporous polymers before and after various modifications. The inset shows the BJH pore size distribution.
Figure S4  FE-SEM images of a) FDU-14-Pd and b) FDU-15-Pd.

**Scanning electron microscopy (SEM) analysis.** FDU-14-Pd consisted of round-shaped particles, while FDU-15-Pd consisted of uniformly gyroidal rod-type crystals. The morphology was very similar to mesoporous silica with the cubic and hexagonal structure, respectively.

Figure S5 Application of hot filtration to the FDU-Pd catalyzed Heck reaction.

**Heck reaction conditions.** Iodobenzene (10 mmol), ethyl acrylate (12 mmol), and triethylamine (NEt₃) (12 mmol) was added to 10 mL of dimethylformamide (DMF). The FDU-Pd catalyst (0.028 mol%) was added to above mixture and stirred in air. The reaction stopped once the catalyst was removed out of the system.
Figure S6 TEM image of FDU-15-Pd catalyst after sixth run in Heck reaction.

The Pd nanoparticles remained inside the hexagonal channels of mesopolymer, and showed no obvious aggregation.

Figure S7 The kinetic curves for allyl alcohol conversion and 1-propanol selectivity in allyl alcohol hydrogenation over FDU-Pd catalyst.

Hydrogenation reaction conditions. Allyl alcohol (10 mmol), FDU-Pd catalyst (0.056 mol %), methanol (50 mL), and H₂ (1 atm). The only byproduct was acetone. The hydrogenation occurred rapidly with reaction time.
Figure S8 The reuse of FDU-Pd and effect of catalyst removal on the hydrogenation.

**Hydrogenation reaction conditions.** No obvious deactivation was observed after the reuse for 4 cycles. The reaction stopped once the catalyst was removed out of the system.