Abstract: The efficient hydrogenation of N-heterocycles with H\(_2\) under mild conditions remains a significant challenge. In this work, polyphosphazene (PZs) microspheres, novel organic–inorganic hybrid materials possessing unique –P=N– structural units and a diverse range of side groups, were used to serve as support for the design of a stable and efficient Pd nanocatalyst (Pd/PZs). The PZs microspheres were prepared by self-assembly induced by precipitation polymerization, and Pd nanoparticles were grown and loaded on the support by a chemical reduction process. Several characterization techniques, including XRD, FTIR, SEM, TEM, XPS, BET and TGA, were used to study the structural features of the nanocomposites. The results revealed that Pd nanoparticles were uniformly distributed on the PZs microspheres, with primary sizes ranging from 4 to 9 nm based on the abundance of functional P/N/O groups in PZs. Remarkably high catalytic activity and stability were observed for the hydrogenation of quinoline compounds using the Pd/PZs nanocatalyst under mild conditions. Rates of 98.9% quinoline conversion and 98.5% 1,2,3,4-tetrahydroquinoline selectivity could be achieved at a low H\(_2\) pressure (1.5 bar) and temperature (40 °C). A possible reaction mechanism for quinoline hydrogenation over Pd/PZs was proposed. This work presents an innovative approach utilizing a Pd-based nanocatalyst for highly efficient multifunctional hydrogenation.

Keywords: polyphosphazene microspheres; Pd nanoparticles; catalysis; quinoline hydrogenation

1. Introduction

Catalytic hydrogenation reactions are a crucial step in the production of various fine chemicals and pharmaceuticals in industry. Quinoline and its derivative compounds, which are a kind of N-heterocycles, are commonly found in natural products and pharmaceuticals [1–3]. The direct hydrogenation of quinolines using H\(_2\) is considered as the most convenient and atom-efficient strategy to obtain the corresponding reduction products [4]. Nevertheless, this hydrogenation process often requires harsh reaction conditions with significant safety risks [5]. Additionally, as illustrated in Scheme 1, the quinoline hydrogenation process may involve a competitive hydrogenation of both benzene rings and heterocyclic rings, leading to the formation of multiple hydrogenated products, e.g., 1,2,3,4-Tetrahydroquinoline (py-THQ), 5,6,7,8-tetrahydroquinoline (bz-THQ), and decahydroquinoline (DHQ) [6]. N-heterocycles, including quinolines and their hydrogenated forms, exhibit strong coordination ability with metal active nanoparticles, which can potentially poison metal catalysts. Therefore, achieving selective hydrogenation of N-containing aromatics remains a challenging task. From an environmental perspective and emphasizing safety considerations, it is imperative to develop an effective and highly chemoselective hydrogenation system that performs under mild conditions.
Catalysts 2024, 14, x FOR PEER REVIEW... Metal catalysts play a pivotal role in industrial applications of hydrogenation reactions. The hydrogenation of N-heteroarenes can be achieved using a variety of homogeneous and heterogeneous transition metal catalysts [7–12]. Numerous homogeneous metal catalysts (e.g., Pd, Ru, Rh) have demonstrated the ability to catalyze the conversion of quinoline into py-THQ. However, they typically require high H2 pressure, elevated temperatures (>100 °C), prolonged reaction times, or harsh additives (e.g., acid, I2, or PPh3) for efficient transformation [13–16]. Moreover, the challenging separation and recovery processes as well as the limited reusability further hinder their practical application. To overcome these limitations, substantial endeavors have been devoted to developing novel heterogeneous metal catalysts for quinoline hydrogenation [4,5,8,10,17]. A series of transition metal supported catalysts, such as M/Al2O3 (M = Pd, Ru or Rh) [18], Pd/hydroxyapatites [19], Rh/montmorillonite [20], polymer-supported Pd catalyst (Pd-pol) [21], and Co3Cu1Ox [22], have been explored for reducing quinolines. However, most of these catalytic systems still require drastic reaction conditions (60–130 °C, 1–4 MPa H2) or rely on expensive carbon nitride supports, which involve complicated synthesis steps and harsh conditions, to obtain a high conversion of quinoline towards py-THQ (Table S1). Among these active metals, Pd nanocatalysts have garnered considerable attention due to their excellent performance in the transformation [18,19,21]. Hence, there is a need to develop efficient and stable Pd-based nanocatalysts which are active in low-pressure H2 and low-temperature systems.

The catalytic activity of noble metal catalysts is strongly related to their particle size and dispersion. Noble metal nanocatalysts of small size and with high dispersion universally display outstanding catalytic hydrogenation performance for quantum size effects [23,24]. However, because of the high surface energy, small-size metallic nanoparticles are prone to aggregate during the preparation process, resulting in reduced catalytic activity and selectivity [25]. Therefore, a variety of supports, such as TiO2, ZnO, SiO2, carbon materials with different morphologies, graphitic carbon nitride, and organic polymers, have been applied to stabilize the metal nanoparticles [26–32]. Among them, as a novel organic–inorganic hybrid materials, polyphosphazenes (PZs) have unique –P=N– structural units with alternating P and N atoms in the backbone and a structural multiplicity of side groups, such as organic, organometallic or inorganic units [33]. The polymers have the characteristics of flexible molecular design, high thermal stability and biocompatibility, which makes them suitable candidates for immobilizing metal particles and biomedical carriers. For instance, Wang et al. and others showed that polyphosphazene nanotubes could be chemically anchored to Ag or Ag-Au nanoparticles via the phosphazene ring and –OH groups and displayed high catalytic performance in the hydrogenation of 4-nitrobenzene [34–36]. However, so far, superior applications of polyphosphazenes as catalyst supports for hydrogenation reactions are still in their infancy.

In this work, a novel Pd nanocatalyst was constructed by using poly-(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) microspheres as a good scaffold for Pd
nanoparticles. The PZs microspheres, as a typical crosslinked polymer, provided abundant phosphazene rings, S=O groups and hydroxyl groups to stably immobilize the Pd active sites by the chemical reduction method with NaBH₄ as the reductant. The Pd nanocatalyst was applied in the direct catalytic hydrogenation of quinoline compounds under mild conditions and it exhibited outstanding catalytic activity and reusability at low temperatures of 30–50 °C and a low H₂ pressure of 1.5 bar. The possible reaction mechanism for quinoline hydrogenation was proposed. This work constructed a high-performance Pd nanocatalyst for N-heterocycles hydrogenation by using a crosslinked polymer with facile synthesis and high chemical stability as the support, contributing to the development of green and sustainable chemistry.

2. Results and Discussion
2.1. Fabrication Process of the Pd/PZs Catalyst

Scheme 2 shows the fabrication procedure of the Pd/PZs nanocatalysts, involving the precipitation polymerization of hexachlorocyclotriphosphazene (HCCP) and 4,4′-sulfonyldiphenol (BPS), with triethylamine (TEA) as the acid acceptor and the chemical reduction of the Pd precursor with NaBH₄ as the reductant. In the first step, HCCP and BPS were used as comonomers and dissolved in acetonitrile. The PZs microspheres were obtained through self-assembly induced by precipitation polymerization between HCCP and BPS after adding TEA to neutralize acid ions. In the second step, PdCl₂ was dissolved in a dilute hydrochloric acid solution to form H₂PdCl₄ before use. The PZs microspheres were mixed with H₂PdCl₄ solution, and PdCl₂²⁻ ions were adsorbed on the surface of the PZs microspheres. Then, the Pd nanoparticles were grown and loaded on the surface of PZs microspheres by in situ reduction of PdCl₂²⁻, with NaBH₄ as the reductant, to yield the Pd/PZs nanocatalyst. The rich phosphazene rings and O-anchoring sites would help the adsorption and confinement of Pd nanoparticles on the PZs support [34]. Unless otherwise specified, the initial Pd loading in the Pd/PZs was 5% in this work.

![Scheme 2. The fabrication procedure of the Pd/PZs composites (top). The polycondensation of the comonomers HCCP and BPS and the crosslinked structure of the PZs (bottom).](image)

2.2. Composition and Structure

The phase structure of the PZs and 5%Pd/PZs samples were studied by XRD. Figure 1 shows that there was one broad peak at around 15° in the PZs polymer, attributable to the amorphous PZs matrix. The intensity of the PZs peak in the 5%Pd/PZs was much weaker than that in the PZs, which might be caused by the partial coverage of Pd particles on the surface of PZs. Apart from the PZs peak, several diffraction peaks at 39.4°, 45.2°,
and 66.4° were also found in 5%Pd/PZs, corresponding to the (111), (200), and (220) lattice planes of the face-centered cubic crystalline structure of metallic Pd [37]. Based on the Scherrer equation, the crystallite sizes of Pd\(^0\) particles in the 5%Pd/PZs were about 4.5 nm. The Pd content in the 5%Pd/PZs, determined by ICP, was about 3.8%. This result implies that PZs can act as an excellent scaffold to anchor Pd nanoparticles of small size.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of 5%Pd/PZs and PZs samples.

The FTIR spectra in Figure 2 confirmed the presence of abundant functional groups on the surface of the PZs and Pd/PZs. Similar adsorption bands appeared in the spectra of the PZs and Pd/PZs. The broad band at 3427 cm\(^{-1}\) was assigned to \(\text{O}--\text{H}\) groups. The bands at 1323, 1290, and 1150 cm\(^{-1}\) belonged to the characteristic O=S=O absorption in the sulfonyldiphenol units [34]. The band at 1200 cm\(^{-1}\) corresponded to P=N bonds in the cyclotriphosphazene structure, while the band at 1014 cm\(^{-1}\) was ascribed to the P–O bond [33,38]. The band at 1373 cm\(^{-1}\) might be related to C=O-P groups. The presence of O=S=O and P–O bands confirmed successful condensation between HCCI and BPS to form PZs. The band at 1587 and 1488 cm\(^{-1}\) could be ascribed to \(--\text{C}=\text{C}--\) in the benzene ring. The bands at 3420, 1405 and 1105 cm\(^{-1}\) indicated the existence of abundant C–OH groups in the PZs. The FTIR spectra of PZs and Pd/PZs were in agreement with the characteristic absorption bands of the PZs microspheres.

![Figure 2](image2.png)

**Figure 2.** FTIR spectra of the 5%Pd/PZs and PZs samples.
The pore structure of 5%Pd/PZs was measured by N$_2$ adsorption/desorption measurement. As presented in Figure S1, the Pd/PZs displayed a type-III adsorption curve without an obvious hysteresis ring, indicating little pore structure in the PZs microspheres. A certain amount of N$_2$ adsorption was observed in the relative pressure range of p/p$_0$ > 0.8, suggesting the existence of an external surface area. The Brunauer–Emmett–Teller (BET) surface area and pore volume of the Pd/PZs were 7.1 m$^2$ g$^{-1}$ and 0.033 cm$^3$ g$^{-1}$, respectively. The morphological features of PZs and 5%Pd/PZs were examined by SEM and TEM. The typical SEM images in the Figure 3a,b show the uniform spherical shapes with a smooth surface and a 500–1000 nm diameter that could be observed in the PZs. The TEM images in Figure 3c–e reveal that most of the Pd nanoparticles with a primary diameter of about 4–9 nm were evenly deposited on the surface of the PZs microspheres without obvious aggregation. The HRTEM picture (Figure 3f) shows the presence of a Pd (111) plane d-spacing of 0.23 nm, supporting the formation of metallic Pd nanoparticles on the surface of the PZs microspheres.

The high resolution XPS spectra of Pd 3d in Figure 4b shows that there were four peaks in the Pd/PZs catalyst. The two peaks at 336.3 and 341.5 eV belonged to Pd$^0$, and the other two peaks at 337.9 and 343.1 eV were assigned to Pd$^{2+}$, respectively [24]. The atomic ratios of Pd$^0$ and Pd$^{2+}$ in the total Pd species are 34.3% and 65.7%, respectively. The Pd$^{2+}$ species might be anchored on PZs by Pd–N or Pd–O bonds.

Figure 4c displays the C 1s XPS spectra of the PZs and Pd/PZs samples. The C 1s spectra of both PZs and Pd/PZs possessed four similar peaks at 284.6, 285.0, 285.7, and 286.6 eV, attributable to C–C, C–O–P, C–N, and C=C groups, respectively [38]. In the N 1s spectra in Figure 4d, two peaks at 298.3 and 397.5 eV could be fitted in the PZs sample, which were assigned to N–P/N=P groups in the cyclotriphosphazene structure and N–C groups, respectively [38]. Compared to the PZs sample, Pd/PZs had two similar peaks for the N–P/N=P and N–C groups, while the N–P/N=P peak shifted 0.1 eV to a higher binding energy, implying the formation of strong ligand bonds between PZs and Pd nanoparticles. Thus, Pd might be anchored on the PZs support by the coordination of Pd–N bonding.

In the P 2p spectra in Figure 4e, two similar peaks at 133.7 and 134.2 eV, belonging to P–N/P=N and P–O groups, were observed in both the PZs and Pd/PZs samples [38]. Figure 4f reflects that the PZs and Pd/PZs samples had three similar oxygen species at 531.9, 533.4 and 534.8 eV, which were related to the C–O group, surface hydroxyl species (OH), and S=O group, respectively [38,39]. Compared to the PZs support, the binding
energy of the OH group and S=O group peaks in the Pd/PZs sample shifted positively about 0.1–0.2 eV, suggesting that the OH and S=O groups also contribute to the coordination behavior of Pd nanoparticles and PZs microspheres. Thus, the phosphazene rings, OH groups and S=O groups might serve as the primary anchoring sites to bond Pd species.

The thermal behaviors of Pd/PZs and PZs were studied by using thermo-gravimetric analysis (TGA). Figure 5 shows the TGA curves of the PZs polymer and 5%Pd/PZs under N\(_2\) atmosphere. A dramatic weight loss was observed in the pure PZs in the temperature range of 470–580 °C, attributable to the decomposition of the polymer framework [38].

Figure 4. (a) XPS survey spectrum of 5%Pt/PZs catalyst; high resolution XPS spectra of (b) Pd 3d, (c) C 1s, (d) N 1s, (e) P 2p, and (f) O 1s.
The loading of Pd did not change the initial decomposition temperature of the polymer, suggesting the high thermal stability of Pd/PZs. It should be noted that the 5%Pd/PZs nanocomposites had a weight loss of 9.5% at 70–200 °C, which might have arisen from the adsorbed water. These results indicate that the Pd nanoparticles loading enhanced the water absorbance of PZs. This is consistent with a similar phenomenon reported previously [38].

![Figure 5. TGA curve of PZs and 5%Pd/PZs under N$_2$ atmosphere.](image)

### 2.3. Catalytic Performance of the Pd/PZs Catalyst

To determine the catalytic behavior of the Pd/PZs catalyst, the catalytic performance for quinoline hydrogenation towards py-THQ was conducted in ethanol. The reactions were first carried out at 40 °C and 1.5 bar H$_2$ for 2 h. As presented in Table 1, little quinoline was converted with PZs support, reflecting that PZs support had no catalytic hydrogenation activity for quinoline hydrogenation under mild conditions. Under the same conditions, 1%Pd/PZs could convert 6.4% of quinoline, with 97.2% py-THQ selectivity. When the Pd loading increased to 5%, the conversion increased to 67.3% for 2 h and maintained high selectivity towards py-THQ (>98%). Extending the reaction time to 4 h, the quinoline was almost completely transformed into py-THQ, with 98.9% conversion and 98.5% py-THQ selectivity. These results indicate that Pd/PZs could effectively catalyze the hydrogenation reaction of quinoline towards py-THQ. In comparison, the 5%Pd/C catalyst had a higher catalytic activity than 5%Pd/PZs, with 99% conversion for 2 h, but a lower selectivity of py-THQ (80.2%). The by-products bz-THQ (2.1%) and DHQ (17.3%) were also formed via the benzene ring hydrogenation. These results reveal that the properties of the support strongly impact the product distribution of Pd catalysts. There might be a strong synergetic effect of Pd and PZs in the chemoselective hydrogenation of quinoline towards py-THQ.

### Table 1. Catalytic activity of quinoline hydrogenation over various catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Samples</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Con. (%)</th>
<th>Sel. (%)</th>
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<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>1%Pd/PZs</td>
<td>40</td>
<td>2</td>
<td>6.4</td>
<td>97.2</td>
</tr>
<tr>
<td>3</td>
<td>5%Pd/PZs</td>
<td>40</td>
<td>2</td>
<td>67.3</td>
<td>98.2</td>
</tr>
<tr>
<td>4</td>
<td>5%Pd/PZs</td>
<td>40</td>
<td>4</td>
<td>98.9</td>
<td>98.5</td>
</tr>
<tr>
<td>5</td>
<td>5%Pd/C</td>
<td>40</td>
<td>2</td>
<td>99.0</td>
<td>80.2</td>
</tr>
<tr>
<td>6</td>
<td>5%Pd/PZs</td>
<td>30</td>
<td>2</td>
<td>41.8</td>
<td>98.5</td>
</tr>
<tr>
<td>7</td>
<td>5%Pd/PZs</td>
<td>40</td>
<td>2</td>
<td>67.3</td>
<td>98.2</td>
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<tr>
<td>8</td>
<td>5%Pd/PZs</td>
<td>50</td>
<td>2</td>
<td>92.7</td>
<td>96.9</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 mmol quinoline, 65 mg catalyst, 1.5 bar H$_2$, 10 mL ethanol.
To establish the optimal reaction conditions, the effects of reaction parameters, including reaction temperature, reaction time, and solvent, on the catalytic activity of 5%Pd/PZs were investigated in detail. The reaction rate was sensitive to reaction temperature. When varying the reaction temperature from 30 °C to 40 °C, the conversion of quinoline improved significantly from 41.8% to 67.9%, along with a high py-THQ selectivity above 98%. When increasing the temperature to 50 °C, the conversion increased to 97.2%, but the py-THQ selectivity reduced to 96.9%. Therefore, 40 °C was chosen in most reactions in this work. Figure 6 shows the results of quinoline hydrogenation for different times over a 5%Pd/PZs catalyst. At the beginning of the reaction, quinoline was converted to py-THQ by the selective hydrogenation of the heterocyclic ring, while little bz-THQ or DHQ was formed by hydrogenation of the benzene ring. When the reaction continued for 0.5 h, 33.1% of the quinoline was mostly converted into py-THQ. As the reaction continued, the conversion gradually increased from 33.1% to 98.9% at 4 h, while maintaining the high selectivity of py-THQ (>98%). Further extending the time to 5 h, py-THQ selectivity was still maintained at >98%. These results suggest that Pd/PZs has a highly catalytic activity and chemoselectivity towards py-THQ under mild conditions.

![Figure 6.](image-url) Conversion and py-THQ selectivity as a function of time at 40 °C using 10 mL ethanol as a solvent over 65 mg 5%Pd/PZs.

As reported before, fewer polar substrates preferred to hydrogenate in more polar solvents in the heterogeneous catalytic system [40]. A series of solvents with different polarities (ethanol, water, tetrahydrofuran (THF), toluene, hexane) were used to investigate the influence of solvent on the reaction rates. As listed in Table 2, the polarity of solvents was in the following order: water > ethanol > THF > toluene > hexane. The reaction rates of Pd/PZs were influenced by the choice of different solvents, but little difference in the py-THQ selectivity (97.9–99.2%) was observed among the five solvents. The conversion of quinoline in the different solvents decreased as follows: toluene > ethanol > hexane > water > THF. Through careful analysis, it was shown that the reaction rates in the various solvents did not correlate with the polarity, which might be due to the higher multipole moments of some solvents [28]. Considering the toxicity of toluene, ethanol was selected for most catalytic reactions in this work.

The recyclability of 5%Pd/PZs catalyst is a crucial factor for industrial application. The catalytic reaction was performed in ethanol at 40 °C and 1.5 bar H₂ for 4 h. After each cycle, the catalyst was recovered, washed with deionized water and ethanol, dried, and then used in the next run. As shown in Figure 7, the conversion did not reduce obviously during the five runs, while py-THQ selectivity kept almost constant (>98%), indicating that the Pd/PZs catalyst was highly stable for the hydrogenation of quinoline in ethanol. The structural properties of the reused Pd/PZs catalyst were characterized by XRD. As
shown in Figure S2, no obvious change was observed in the structure of Pd/PZs after the reaction. The ICP analysis showed that the quantity of Pd leaching into the reaction solution in each run was negligible (<0.02%). These results reveal the good stability of the novel Pd nanocatalyst.

Table 2. Catalytic activity of quinoline hydrogenation over 5%Pd/PZs in different solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Con. (%)</th>
<th>Sel. (%)</th>
<th>Solvent Polarity</th>
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<tr>
<td>1</td>
<td>ethanol</td>
<td>67.3</td>
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</tr>
<tr>
<td>2</td>
<td>water</td>
<td>46.2</td>
<td>99.2</td>
<td>10.2</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>40.3</td>
<td>98.1</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>90.7</td>
<td>97.9</td>
<td>2.4</td>
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<tr>
<td>5</td>
<td>hexane</td>
<td>51.6</td>
<td>98.5</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 mmol quinoline, 65 mg Pd/PZs, 40 °C, 2 h, 1.5 bar H2, 10 mL solvent.

Figure 7. Recycling experiments of the 5%Pd/PZs catalyst under 40 °C and 1.5 bar H2 for 4 h.

2.4. Possible Reaction Pathway

Based on the results mentioned above, a possible reaction pathway for the quinoline hydrogenation over Pd/PZs was proposed. It is considered that the quinoline hydrogenation process catalyzed by Pd/PZs catalyst under H2 might involve the competitive hydrogenation of benzene rings and heterocyclic rings into bz-THQ and py-THQ, as well as a further hydrogenation reaction to form DHQ [28]. In our reaction system, py-THQ was almost the only product in the hydrogenation reaction catalyzed by Pd/PZs, implying that the quinoline hydrogenation reaction is occurring through the exclusive adsorption of the N-heterocycle rather than the benzene ring. As displayed in Scheme 3, initially, the catalytic reaction begins with the adsorption of the quinoline substance on the surface of the PZs support via an interaction between the N-heterocycle of quinoline and –OH groups. At the same time, molecular H2 is adsorbed on the Pd nanoparticles and is activated and decomposed into H atoms. Then the N-heterocycle is attacked by active H atoms to form a hydrogenated N-heterocycle, thus producing py-THQ [27,28]. The N-heterocycle would be more easily hydrogenated by active H atoms at the Pd–PZs interface. Meanwhile, the dissociated hydrogen also might transfer to the surface of the PZs near the Pd–PZs interface to reduce the adsorbed N-heterocycle. Subsequently, py-THQ leaves the surface of the Pd/PZs catalyst quickly with the assistance of the solvent, and a new quinoline molecule fills the vacant space. Hence, the Pd/PZs nanocatalyst is highly active and stable in the controlled transformation of quinolines into py-THQ under low pressure of H2 and low temperature.

The catalytic activity of Pd/PZs might be affected by three factors as follows. Firstly, PZs microspheres have a unique spherical structure, rich phosphazene rings and O-anchoring sites, offering abundant anchoring sites to fix Pd nanoparticles of small size.
Secondly, the rich hydroxyl groups on the surface of PZs would favor adsorption of N-heterocycle of quinoline via the strong interaction between the pyridine ring of quinoline and –OH groups, which might be the primary reason for the high selectivity for py-THQ. Thirdly, the Pd nanocatalyst is effective in the activation of H₂ and the hydrogenation of quinoline to produce py-THQ. In a word, the metal–support synergetic effects between the PZs polymer and Pd nanoparticles contribute to the superior catalytic activity and high py-THQ selectivity of the Pd/PZs catalyst.

![Scheme 3](image)

**Scheme 3.** Possible reaction pathway of quinoline hydrogenation over Pd/PZs.

### 2.5. Hydrogenation of Other N/O/S-Heterocycles Compounds

The Pd/PZs catalyst was not only effective in catalyzing the hydrogenation of quinoline under low pressure of H₂, but also the hydrogenation of various other quinoline compounds, O-heterocycles and S-heterocycles compounds. As presented in Table 3, 6-methylquinoline and 8-methylquinoline were almost completely converted into 6-methyl-1,6,7,8-tetrahydroquinoline and 8-methyl-1,6,7,8-tetrahydroquinoline over Pd/PZs under 40 °C and 1.5 bar H₂ for 6 h, with a high yield above 98%. Pd/PZs gave moderate catalytic activity to transform 2-methylquinoline into 2-methyl-1,6,7,8-tetrahydroquinoline, with 58.3% conversion, and >99% conversion of 2-methyl-1,6,7,8-tetrahydroquinoline, under 60 °C and 1.5 bar H₂ for 4 h. Prolonging the reaction time would enhance the conversions. Pd/PZs was also active in the transformation of 2,3-benzofuran into 2,3-dihydrobenzofuran, with >99% yield under 40 °C and 1.5 bar H₂ for 4 h. When 2,3-benzothiophene was used as substrate, a low conversion (2.6%) was obtained 40 °C and 1.5 bar H₂ for 6 h, but it maintained a high selectivity of the 2,3-dihydrobenzothiophene above 99%. These results confirm that the Pd/PZs nanocatalyst was highly selective in the hydrogenation of N/O/S-heterocycles under mild conditions.

<table>
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<th>Entry</th>
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<td>40</td>
<td>6</td>
<td>2.6</td>
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</tr>
</tbody>
</table>

Reaction conditions: 0.5 mmol substance, 65 mg Pd/PZs, 1.5 bar H₂, 10 mL ethanol.

Table 3. Catalytic activity of the hydrogenation of other N/O/S-heterocycles compounds.
3. Materials and Methods

3.1. Materials

All reagents were purchased from Aladdin and used without further purification. The commercial carbon support was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Activated charcoal) (Shanghai, China).

3.2. Preparation of the Poly-(Cyclotriphosphazene-co-(4,4′-Sulfonyldiphenol)] Microspheres

PZs microspheres were prepared by precipitation polymerization of HCCP and BPS according to procedures reported in the literature. In brief, 3.48 g of HCCP and 7.51 g of BPS was dissolved in 500 mL of acetonitrile. Then, 15 mL of TEA was added to the solution. The obtained mixtures were stirred in an ultrasonic bath at 40 °C for 1 h. Subsequently, the resulting solid was separated from the solution by centrifugation and washed with ethanol and water several times. The solid was dried under a vacuum, giving PZs microspheres in the form of a white powder.

3.3. Preparation of the Pd/PZs Catalyst

The Pd/PZs catalyst was prepared via an ultrasound-assisted reduction method. First, 0.2 g of PZs microspheres was mixed with 20 mL of water. A certain amount of PdCl$_2$ aqueous solution (e.g., 0.1 g Pd/mL, 0.1 mL for 5%Pd/PZs) was added to the aqueous PZs microspheres dispersion and was stirred at room temperature for 30 min. After that, 10 mL of NaBH$_4$ aqueous solution (0.1 mol/L) was added the above mixture dropwise under ultrasonic treatment, resulting in a grayish suspension. The reaction system was treated in an ultrasonic bath for 30 min. The resulting solids were separated by centrifugation and washing with water and then dried at 80 °C in a vacuum oven. The 5%Pd/C was also prepared via a similar process with commercial carbon as support. The size of the Pd nanoparticles, calculated by the Scherrer equation, was about 14.3 nm (Figure S3).

3.4. Catalytic Performance Evaluation

The hydrogenation of quinolines was conducted in a 50 mL stainless-steel autoclave. The experimental procedure was as follows: 0.5 mmol of quinoline, 65 mg of catalyst, and 10 mL of ethanol were injected into the autoclave. The autoclave was flushed with H$_2$ five times to remove the air, stirred at 400 rpm under 1.5 bar H$_2$ and then heated to the desired temperature. After the reaction, the substrate and products were quantified by a gas chromatograph (GC, Shimadzu GC-2010, Kyoto, Japan) with an Agilent capillary column DB-5, and the products were also identified by GC coupled with a mass spectrometer (GC-MS, Shimadzu GCMS-QP2010, Kyoto, Japan). The quantification of products was identified by an external standard method.

The calculation of conversion was as follows:

\[
\text{conversion(\%)} = \frac{n_0 - n'_0}{n_0} \times 100\% \quad (1)
\]

where $n_0$ and $n'_0$ are the initial mol of quinoline added to the reactor and the residual mol of quinoline after the reaction, respectively.

The selectivity of products was calculated by the mol of products and the mol of converted quinoline.

\[
\text{Selectivity of product} = \frac{n(\text{product})}{n_0 - n'_0} \times 100\% \quad (2)
\]

4. Conclusions

We have reported a simple strategy for the fabrication of Pd/PZs nanocomposites by precipitation polymerization and a chemical reduction process. The PZs support offered rich N/O-anchoring sites to anchor stably Pd nanoparticles. Various characterization results revealed that the small-sized Pd nanoparticles were well dispersed on the surface.
of the PZs microspheres. The novel catalyst was found to effectively catalyze quinoline hydrogenation towards py-THQ through the exclusive hydrogenation of the N-heterocycle rather than the benzene ring under mild conditions. The reaction rates could be impacted by many factors, including Pd content, reaction time, reaction temperature, and solvents. An optimal activity with 98.9% conversion and 98.5% py-THQ selectivity was obtained over 5%Pd/PZs under 1.5 bar H₂ and 40 °C for 4 h. The metal–support synergistic effects of metallic Pd and PZs support co-contributed to the outstanding catalytic activity of Pd/PZs in the N-heterocycles hydrogenation reactions. This work provides novel efficient and stable catalysts for the hydrogenation reactions of N-heterocycles under mild conditions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/10.3390/catal14060345/s1. Characterizations; Figure S1: (a) Nitrogen sorption isotherms of 5%Pd/PZs, (b) pore-size distribution curves of 5%Pd/PZs; Figure S2: The XRD pattern of 5%Pd/PZs before and after reaction; Figure S3: XRD pattern of 5%Pd/C sample; Table S1: The comparison of chemoselective hydrogenation of quinoline towards py-THQ with various catalysts [5,8,21,22,28,41–46].

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