ABSTRACT: Porous polymer catalysts possess the potential to combine the advantages of heterogeneous and homogeneous catalysis, namely, easy postreaction recycling and high dispersion of active sites. Here, we designed a −SO\(_3\)H functionalized polyphenylene (PPhen) framework with purely sp\(^3\)-hybridized carbons, which exhibited high activity in the hydration of alkynes including challenging aliphatic substrates such as 1-octyne. The superior property of the structure lies in its covalent crosslink in the xy-plane with a σ-π stacking interaction between the planes, enabling simultaneously high swellability and porosity (653 m\(^2\) g\(^{-1}\)). High acidic site density (2.12 mmol g\(^{-1}\)) was achieved under a mild sulfonation condition. Similar turnover frequencies (0.015 ± 0.001 min\(^{-1}\)) were obtained regardless of acidic density and crosslink content, suggesting high accessibility for all active sites over PPhen.

In addition, the substituted benzene groups can activate alkynes through a T-shape CH/π interaction, as indicated by the 8 and 16 cm\(^{-1}\) red shift of the alkyne C–H stretching peak for phenylacetylene and 1-octyne, respectively, in the infrared (IR) spectra. These advantages render PPhen-SO\(_3\)H a promising candidate as a solid catalyst replacing the highly toxic liquid phase acids such as the mercury salt.

INTRODUCTION

Porous organic materials play an important role in gas storage and separation,\(^1\)−\(^4\) drug release,\(^5\) catalysis, sensing,\(^6\) and membrane separation\(^7\) due to their properties in merging the benefits of porosity, processability, synthesis diversity, and organic nature.\(^8\) A number of novel polymeric frameworks have been developed in recent years,\(^9\)−\(^18\) such as polytriazine,\(^9\)−\(^10\) hyper-cross-link polystyrene (HPS),\(^11\)−\(^12\) nanoporous polydivinylbenzene (PDVB),\(^13\) dihydroxybenzoic acid-based polymer nanospheres,\(^14\) and porphyrin network polymers.\(^15\)−\(^16\)

The polymeric structures not only offer a high surface area and well-controlled porosity but also provide an organic environment, the advantage of lightweight, and a dynamic structure upon external stimulation. Thus, they have offered an innovative way to combine the advantages of homogeneous and heterogeneous catalysis.\(^17\) On one hand, a solvent-like reaction environment is established via organic ligands and the geometric structure of the framework, providing well-dispersed high-density active sites. On the other hand, the heterogeneous nature of solid catalysts facilitates postreaction separation, rendering them environment-friendly alternatives for highly toxic homogeneous liquid catalysts.

Various polymer-based solid acid catalysts have been investigated in the recent years for hydrolysis,\(^18\) hydration,\(^19\)−\(^21\) dehydrogenation,\(^22\)−\(^24\) and other acid-catalyzed reactions,\(^25\)−\(^26\) in both gaseous and liquid phase as the replacement of liquid acids, which leads to severe technical and environmental problems in practical applications. Acid-catalyzed alkyne hydration is a straightforward and atom-economical method for the synthesis of ketones via carboxylation intermediates,\(^27\) where efforts have been paid to replace the traditional highly toxic mercury salt catalysts with recoverable and environment-friendly solid acid catalysts.\(^28\)−\(^29\) A number of attempts have been made in developing polymer-based solid acids; however, their catalytic activity is often limited by the contradiction lying within the nature of the polymeric framework.

A good polymeric heterogeneous catalyst requires high active site density and good accessibility simultaneously, which can be achieved in porous polymers by increasing the porosity and swellability. While the porosity of a polymer generally increases as a function of crosslink content, as seen in sp\(^3\) carbon linker groups,\(^12\) a three-dimensionally crosslinked framework reduces its ability to swell, and thus decreases the accessibility of the active sites. High swellability is usually obtained in polymers with lower crosslink content,\(^30\)−\(^31\) within
Scheme 1. Concept of PPhen Structure Showing the Covalent Crosslinks in xy-Plane (Left), Swelling Along z Axis (Middle), and Activation of C≡C–H (Right) via T-Shape CH/π Interaction.

The scheme is a simplification of the real PPhen-SO3H structure and does not indicate a laminar structure.

which pore formation is difficult due to close stacking of the linear chains. This further hinders the formation of high-density active sites in the polymer matrix. Such a dilemma between high active site density and good molecular accessibility limits the practical application of porous polymers. Here, we hypothesize that the solution to this dilemma lies in the design of a polymer structure with covalent crosslinks at a two-dimensional level. This structure enables pore formation with rigid chemical bonds and pure molecular interactions between crosslinking layers, which provides good swellability, allowing reactant molecules to diffuse into the polymer matrix, which lowers the mass transfer limitation.

To achieve this target, we employed the polyphenylene (PPhen)-based polymeric framework functionalized with −SO3H acidic sites. The material has been investigated previously as the ion-exchange resin, which shows that it can facilitate water diffusion through the hydrophilic regions and possesses a rigid backbone preventing the folding of the structure. All carbon atoms in the PPhen-based polymer are sp2-hybridized, retaining covalent crosslinks in the xy-plane (Scheme 1, left), while π–π stacking becomes the main force at z axis (Scheme 1, middle). As a result, PPhen achieves a high surface area of 653 m2 g−1 and good swellability. Meanwhile, it also provides an organic solvent-like environment for reaction molecules via high density of disubstituted (phenylene) and tetrasubstituted benzene groups, which activate alkynes through the edge-to-face configuration (Scheme 1, right). The catalytic behavior of sulfonated PPhen solid acid is evaluated by the hydration of phenylacetylene and 1-octyne, as a result, PPhen-SO3H shows superior hydration activity even for aliphatic 1-octyne, a reaction that is very challenging for solid acid catalysts. The PPhen-SO3H catalyst has the potential to replace Hg-based catalysts in hydration reactions.

## MATERIALS AND METHODS

### Synthesis of PPhen

To obtain a fully crosslinked PPhen-100% polymer framework, 1,2,4,5-tetrabromobenzene (1.531 g, 3.89 mmol) and benzene-1,4-diboronic acid (1.289 g, 7.78 mmol) were added into 120 mL of dimethylformamide. The mixture was degassed through three freeze–pump–thaw cycles. K2CO3 (2.0 M, 15 mL) and Pd(PPh3)4 (0.3 g, 0.25 mmol) were then added with three subsequent freeze–pump–thaw cycles. The mixture was then purged with Ar and heated to 150 °C for 20 h under stirring. The product precipitated in water and was washed by water, dichloromethane, and methanol. Approximately 600 mg of a gray product was obtained in each batch. PPhen with different crosslink contents were obtained by changing the ratio of 1,2,4,5-tetrabromobenzene and 1,4-dibromobenzene. The reactants used in the synthesis of different polymers are summarized in Table S1.

### Synthesis of PPhen-SO3H Catalysts

As-prepared PPhen polymers were treated with HCl/H2O2 (5:1, v/v) solution to remove Pd residue from the cross-coupling reaction. The mixture was stirred overnight under room temperature and heated up to 60 °C for 2 h. The product was then washed with water and methanol. After drying in a vacuum oven overnight, 200 mg of H2O2-treated polymer was added to 5 mL of concentrated sulfuric acid (98 wt %) and stirred at 40 °C for 16 h. The product was poured into 200 mL of deionized water and filtered, followed by washing with H2O and methanol until neutral pH to eliminate physically absorbed sulfuric acid molecules within the pores. The obtained PPhen-SO3H catalysts were dried in a vacuum oven under 50 °C overnight.

### Hydration Reaction of Alkynes

In a typical reaction, 20 mg of catalyst was added into a glass tube reactor with 1 mL of H2O and 110 μL (1 mmol) of phenylacetylene. Forty microliters (0.176 mmol) of dodecane was also added into the reactor as the standard in the gas chromatography–mass spectrometry (GC–MS) measurement. The standard reaction continued for 24 h at 100 °C. After the reaction, 5 mL of tetrahydrofuran (THF) was added and the mixture was placed in the ultrasonic washer for 30 min. Fifty microliters was taken from the mixture and diluted with THF to be measured with GC–MS for quantification. The conversion of phenylacetylene, yield of acetophenone, and selectivity of catalysts mentioned are summarized in Table S4.
Characterizations. Samples for high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were prepared by sprinkling a small amount of dry sample powder on 400 mesh copper grids with a lacey carbon support film. High-resolution aberration-corrected HAADF-STEM images in Figures 1 and S2 and S4 were acquired on probe-corrected (CEOS) JEM ARM 200CF (JEOL, Japan) operated at 200 keV. We used a 40 μm probe-forming aperture, resulting in 31.8 mrad probe convergence semiangle. The HAADF signal was gathered at 8.0 cm STEM camera length, integrating the scattered electron intensity between 71.5 and 257.8 mrad. Energy-dispersive X-ray spectroscopy (EDS) data were obtained on the probe-corrected JEM ARM 200CF (JEOL, Japan), which is equipped with large solid-angle dual EDS detectors for X-ray spectroscopy and elemental mapping. The EDS data acquisition was carried out in STEM imaging mode, with a probe current of 143 pA (probe size is SC), with the microscope operated at 200 keV acceleration voltage. Each EDS spectrum image is 100 × 100 pixels in size with 0.05 s exposure time per pixel. Gatan Microscopy Suite Software was used for EDS spectrum imaging data acquisition. Nitrogen adsorption−desorption isotherms were recorded at 77 K using a Micromeritics 3Flex surface characterization analyzer. The samples were degassed in vacuum at 200 °C overnight for removal of any contaminants. Specific surface areas were determined according to the BET model.

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Figure 1. (a) Schematic diagram shows the synthesis of PPhen and loading of SO₃H. (b) HAADF-STEM image of PPhen-SO₃H. (c−e), EDS map of carbon (c), sulfur (d), and carbon + sulfur (e). Region difference between STEM and EDS map is due to sample drifting.

Figure 2. (a) N₂ physisorption of fresh PPhen-100% (black), PPhen-100% treated with H₂O₂ (red), and PPhen-SO₃H-100% (orange). (b) Comparison of N₂ physisorption for H₂O₂ treated PPhen-100, PPhen-82, PPhen-65, PPhen-36, and PPhen-0%. (c) Thermogravimetric analysis (TGA) of the corresponding PPhen polymers in (a). (d) TGA and the first derivatives of weight loss for PPhen-SO₃H-100% and PPhen-SO₃H-0%.

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Acidic site densities of as-synthesized PPhen-SO₃H catalysts and Amberlyst 15 are measured via chemical titration. Fifty milligrams of the catalyst is added to 50 mL of 0.01 mol·L⁻¹ NaHCO₃ solution and stirred for 24 h. The mixture was filtered to get a clear solution, which is then titrated with 0.01 mol·L⁻¹ HCl solution to get the amount of remaining NaHCO₃. The concentration of the HCl standard solution is determined by the titration with dry Na₂CO₃ standard. The concentration of NaHCO₃ is then titrated with HCl standard solution. NaHCO₃ is chosen because the scale of cross section for HCO₃⁻ ions (3.0 Å) is comparable to the reactants phenylacetylene (4.3 Å) and 1-octyne (1.7 Å) (estimated from the bond length in Lange’s Handbook of Chemistry). Further, considering the nonpolar interaction between the reactants and organic substrate of polymer, the acidic sites included in the titration should be accessible to the reactants.

Thermogravimetric analysis (TGA) was measured on PerkinElmer Pyris 1 TGA. 2−10 mg of the sample is heated from 30 to 700 °C with a heating rate of 10 °C·min⁻¹. Attenuated total reflection infrared (ATR-IR) spectroscopy is measured with Bruker α FTIR spectrometer. The spectra were taken within the 4000−400 cm⁻¹ range. The spectra of polymers absorbed with phenylacetylene were taken with 10 mg of polymers absorbed with 5 μL of phenylacetylene.
RESULTS AND DISCUSSION

PPhen-SO$_3$H Catalysts: Structure and Chemical Properties. PPhen is synthesized through the palladium-catalyzed cross-coupling reaction of 1,2,4,5-tetrabromobenzene and benzene-1,4-dibromobenzene as reported previously. To study the role of crosslink content in catalysis, 1,2,4,5-tetrabromobenzene is selectively replaced with 1,4-dibromobenzene. This results in a controlled ratio between phenylene and tetrasubstituted benzene groups in the PPhen framework and thus determines the crosslink content, which is denoted as PPhen-SO$_3$-X%, where X% is the normalized crosslink content (Table S1, Supporting Information). To avoid the influence of Lewis acidity of Pd in the hydration reactions, as-prepared PPhen is treated with H$_2$O$_2$−HCl to remove the Pd residue (Figure 1a). −SO$_3$H sites are introduced by treating PPhen with concentrated sulfuric acid (95−97%) (Figure 1a), the duration of which decides the acidic site density over the fully crosslinked polymer (PPhen-SO$_3$-H-100%). The crosslinked polymer has irregular shapes in the form of curved aggregates (Figure S1, Supporting Information). High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) images show the candy floss shape of the polymer particles in the range of 100−400 nm (Figures 1b and S2, Supporting Information). −SO$_3$H sites disperse uniformly across the PPhen framework, as confirmed by energy-dispersive X-ray spectroscopy (EDS) element mapping of C and S (Figures 1c−e and S3, Supporting Information). The linear polymer (PPhen-SO$_3$-H-0%) has very similar morphology and −SO$_3$H distributions (Figure S4, Supporting Information). PPhen-SO$_3$-H-100% shows an amorphous structure, as indicated in the X-ray diffraction (XRD) measurement (Figure S5, Supporting Information). The absence of a Pd signal in the EDS spectrum and the XRD pattern confirms the complete removal of Pd residues.

The uptake−desorption isotherm of fresh fully crosslinked PPhen (PPhen-100%) (Figure 2a, black) shows a type I shape of isotherm, corresponding with microporous materials. The increase in adsorbed volume between 0.2 and 0.8 P/P$_0$ indicates a large external surface, contributing to roughly 10% of the BET-equivalent specific surface area. Though BET surface area calculations are not representative for microporous materials, here, they are used to make a relative comparison between different PPhen systems. The steep increase of P/P$_0$ = 0.9 stems from the interparticulate void. The removal of the Pd residues by H$_2$O$_2$ not only reduces the weight of PPhen but also creates new pores and voids, which boosts the uptake surface areas to 435, 407, 224, and 36 m$^2$g$^1$ for PPhen-82, PPhen-65, PPhen-36, and PPhen-0%, respectively (Figure 2b and Table S1, Supporting Information). In contrast to PPhen-100%, the surface area of PPhen-0% increases from 36 to 76 m$^2$g$^{-1}$ after sulfonation (Figure S6 and Table S2, Supporting Information). This is possibly due to the increased repulsive force between −SO$_3$H sites in linear chains, creating new pore systems.

The PPhen polymer framework shows outstanding thermal stability (Figure 2c, red) with an initial decomposing temperature of 400 °C. PPhen-SO$_3$H-100% undergoes rapid weight loss (11%) below 100 °C due to the evaporation of hydrogen-bonded H$_2$O at −SO$_3$H sites. At 200 °C, −SO$_3$H starts to decompose and reaches the highest rate of weight loss at around 400 °C, as indicated by the peak in the first derivatives of TGA (Figures 2d and S7, Supporting Information). The weight loss in this region (16%) is well-matched with the 1.81 mmol·g$^{-1}$ acidic site density (corresponding to 14.5 wt % −SO$_3$H) measured by chemical titration (Table S2, Supporting Information). Compared with the commercial catalyst Amberlyst 15, which lost all −SO$_3$H sites below 350 °C, the superior thermal stability of PPhen-SO$_3$-H-100% enables reactions catalyzed at higher temperatures. The decomposition of −SO$_3$H in PPhen-SO$_3$H-0% starts at 280 °C, which is 80 °C higher than that of PPhen-SO$_3$-H-100% (Figure 2d). The results agree with the literature that the stability of −SO$_3$H increases with the decrease in crosslink content.26 There is no obvious water evaporation for PPhen-SO$_3$H-0%, possibly due to its low acidic site density (0.48 mmol·g$^{-1}$) and porosity (76 m$^2$g$^{-1}$).

The structural changes from fresh PPhen to PPhen-SO$_3$H are characterized by attenuated total reflection infrared (ATR-IR) spectroscopy for fully crosslink polymer (Figure 3) and linear polymer (Figure S8, Supporting Information). The absorption bands at around 3030 cm$^{-1}$ in all spectra represent the aromatic C−H stretch. The successful loading of −SO$_3$H sites is confirmed by the new peaks at 1032 and 1100 cm$^{-1}$, corresponding to the S=O stretching.26,43,46 The emergence of O−H stretching (3400 cm$^{-1}$) and O−H bending (610, 1650 cm$^{-1}$) bands for PPhen-SO$_3$H-100% shows the absorbance of H$_2$O molecules via hydrogen bonds.45-46 This IR feature of H$_2$O is consistent with the H$_2$O loss in the TGA measurement, which shows H$_2$O loss of around 3.3 per
PPhen-SO$_3$H catalysts show an increase in phenylacetylene conversion from 23 to 80% when the surface area increases from 36 to 653 m$^2$g$^{-1}$, corresponding to an increase in crosslink content from 0 to 100% (Figure 4c). Similarly, the yield of acetophenone increases from 13 to 67%. The positive relationship between activity and crosslink content is different from conventional polymeric solid acid systems, in which catalysts with less crosslink content usually have higher activity due to the flexibility of the polymer frameworks, which allows the diffusion of reactants and products. 

Catalytic Performance of PPhen-SO$_3$H in Phenylacetylene Hydration. We first studied the structure-reactivity relationship through the hydration of aromatic alkyne phenylacetylene. The conversion of phenylacetylene and the yield of acetophenone are 22 and 16%, respectively, for PPhen-SO$_3$H-100% at 100 ºC over 2 h, which is 20 times higher than that of the macromeretric resin Amberlyst 15 (20–30 mesh) (Figure 4a and Table S3). Both conversion and yield gradually increase, reaching 80 and 67% at 24 h, respectively. Overall, over 80% of selectivity is achieved between 40 and 80% conversion for PPhen-SO$_3$H-100%, showing superior hydration performance (Figure 4b). Ninety-five percent conversion and selectivity is reached when increasing the temperature to 120 ºC. The catalytic activities of the commercial gel-type resins are also evaluated under the same reaction conditions. The conversions of phenylacetylene are 52, 15, and 20% for three chosen resins (Dowex 50WX2, Dowex G26, Dowex Marathon), respectively (Table S4, Supporting Information), which again shows the potential of PPhen-SO$_3$H as a promising solid acid.

PPhen-SO$_3$H ligands. All of the vibrational modes are also visible in the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) (Figure S9). The solid-state $^{13}$C NMR spectrum of PPhen shows two signals at 140.1 and 129.2 ppm in the characteristic region of sp$^2$ carbon atoms, which correspond to the connecting (140.1 ppm) and nonconnecting (129.2 ppm) carbons in the substituted benzene groups (Figure 3b). Although not well distinguished due to large band width, both peaks shift toward the middle after sulfonation by 0.4 to 139.7 and 129.6 ppm, respectively, suggesting the emergence of an NMR signal for aromatic carbon coordinated with −SO$_3$H ligands.

Alkyne Activation over PPhen. PPhen-SO$_3$H catalysts also benefit from a high density of phenylene and tetrasubstituted benzene groups, for which the interaction with alkynes is studied via infrared spectra (Figure 5) by absorbing a small number of reactants within the PPhen-SO$_3$H catalysts (Figure 5a). The peaks for C≡C bond (2100–2260 cm$^{-1}$) are difficult to identify due to weak intensity, while alkyl C–H stretching is identified at around 3289 cm$^{-1}$ for pure phenylacetylene. It is red-shifted to 3281 cm$^{-1}$ for...
phenylacetylene over both PPhen-SO$_3$H-100% and PPhen-SO$_3$H-0%. In comparison, the alkyne C–H stretching of phenylacetylene over Amberlyst 15 remains at 3289 cm$^{-1}$. This effect can be understood as the interaction between the substituted benzene groups in the PPhen and the aromatic alkyne in Amberlyst 15 with an edge-to-face (T-shape) configuration (Scheme 1, right), in which phenylacetylene is vertically adsorbed on the alkylnyl group (−C≡C–H) pointing to the substituted benzene group to minimize the repulsive force with the adjacent framework benzene groups. As a result, the C≡C bond is weakened and shifts the alkyne C–H peak toward a lower frequency region. The existence of this configuration is rationalized by research on the CH/π interaction between benzene and hydrocarbons, which showed the preference of C–H bonds for pointing toward the benzene ring and that the benzene–acetylene complex bore the strongest interaction among all complexes studied.$^{35}$ The high density of phenylene and tetrasubstituted benzene groups in PPhen-SO$_3$H catalysts maximizes such absorption and activation of phenylacetylene.

In addition, PPhen-SO$_3$H can be well dispersed in water, in which the hydrophilicity of the −SO$_3$-H group and hydrophobicity of the PPhen framework (Figure S11 and Movies S1 and S2, Supporting Information) enable the simultaneous adsorption of H$_2$O and alkynes. This creates a “solvent-like” environment, which enables alkynes to accumulate around the surface of PPhen and facilitates the subsequent reaction with hydrogen-bonded water at −SO$_3$-H sites. The excess amount of water will further dilute the local concentration of the product ketone as it is more soluble than alkynes and drive the reaction forward.

**Hydration of Aliphatic Alkynes.** The CH/π interaction is not limited to aromatic alkynes, as it is proposed by studies on direct interaction between aliphatic substituents and the counterpart aromatic groups.$^{31–36}$ Therefore, we propose that PPhen-SO$_3$H can also activate aliphatic alkynes. The hydration of 1-octyne was studied with PPhen-SO$_3$H-100% catalysts with the highest acidic site density (2.12 mmol·g$^{-1}$) and Amberlyst 15 (2.4 mmol·g$^{-1}$). PPhen-SO$_3$H-100% obtains a conversion of 51% and a yield of 30% as expected, while Amberlyst 15 shows almost no activity toward the hydration of the aliphatic alkyne (Figure 6a), again showing the exceptional activation of alkynes over a PPhen framework. The reduced activity compared with the phenylacetylene substrate can be understood as the lack of the conjugation between phenyl and C≡C groups, which activate the C≡C in phenylacetylene. The interaction between the PPhen framework and 1-octyne is also studied with ATR-IR (Figures 6b and S12, Supporting Information), which shows a red shift of the C–H stretching peak from 3309 cm$^{-1}$ for pure 1-octyne and that adsorbed in Amberlyst 15 to 3293 cm$^{-1}$.

**CONCLUSIONS**

SO$_3$H-group functionalized PPhen is designed with adjustable crosslink contents and acidic site densities. The advancement of such catalysts features high porosity, which allows environment-friendly synthesis using a mild sulfonation process, as well as excellent swellability, which ensures accessibility of all acidic sites in the pores. The phenylene and tetrasubstituted benzene groups can activate reactants through CH/π interactions with a T-shape configuration and provide “an organic solvent-like environment”. Being able to activate aliphatic C≡C under mild conditions, PPhen-SO$_3$H serves as a promising candidate for alkyne chemistry in the replacement of highly toxic liquid acids in the synthesis of valuable chemicals.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01763.

Calculation of TOF, acidic site density, and crosslink content; characterizations of PPhen-SO$_3$H-0% and PPhen-SO$_3$H-100%; catalytic performance of PPhen-SO$_3$H and commercial acidic resins (PDF)
Hydrophobicity of PPhen, Movie S1_S-PPhen (MP4)
Hydrophobicity of PPhen-SO$_3$H, Movie S2_PPhen (MP4)

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Notes
The authors declare no competing financial interest.

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