



# Ruthenium Inlaying Porous Aromatic Framework for Hydrogen Generation From Ammonia Borane

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Porous organic frameworks (POFs) are a new family of porous materials, which are characterized by high chemical and thermal stabilities, structural design-abilities, chemical functionalities, high porosities, etc. Designable skeletons of POFs lead to different applications in many fields. Herein, we report a porous aromatic framework PAF-72 synthesized *via* ionothermal reaction. The inherently nitrogen contained skeleton of PAF-72 is beneficial for introducing catalytic active center Ruthenium, which is verified by ICP, TGA, and TEM element mapping. Besides, Ru/PAF-72 shows excellent activity in hydrogen generation from hydrolysis of ammonia borane and good cyclic performance.

**Keywords:** porous organic framework, ionothermal reaction, ammonia borane, Ruthenium, catalytic hydrolysis

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## INTRODUCTION

Hydrogen is the most abundant element on earth and the molecular hydrogen gas, H<sub>2</sub>, is one of the cleanest energies we can utilize (Schlapbach and Züttel, 2001). The product of combustion is water, which is also environmentally friendly. However, the storage and transportation remain as the main problems for hydrogen energy, which restrict its development considerably. Hydrogen storage materials, such as chemical hydride, adsorption of hydrogen storage material, and metal hydride have been widely studied in recent years (Züttel, 2003; Graetz, 2009). Ammonia borane (AB), which has high stability and high hydrogen content (19.6 wt% and 146 g L<sup>-1</sup>), makes it as a potential and ideal hydrogen storage material (Peng and Chen, 2008; Rossin and Peruzzini, 2016). Hydrogen can be released from AB by pyrolysis or hydrolysis process. Pyrolysis usually happens at high temperature conditions with accompanying by-products (Hu et al., 1978; Frueh et al., 2011). In contrast, hydrolysis happens under mild conditions, and metal catalysts can accelerate the procedure (Fu et al., 2018; Chen et al., 2019). The aggregation of metal catalysts is a main problem that can decrease the activity of catalysis and cyclic utilization (Zhang et al., 2018). So, it is helpful to disperse the metal catalyst in porous frameworks and anchor them in a skeleton (Qin et al., 2018).

From the last decade, porous organic frameworks (POFs), which are usually constructed from wholly organic building units, have enjoyed a good development because of their high stability, structural design-abilities, chemical functionalities, and high porosities (Zhu and Ren, 2015; Das et al., 2017; Tan and Tan, 2017). Current investigations have demonstrated that POFs are promising materials in many fields, such as gas storage, separation, heterogeneous catalysis, and sensors. Since the polymers of intrinsic microporosity (PIM) was reported by Budd et al. (2004), the covalent organic frameworks (COFs) (Cote et al., 2005; El-Kaderi et al., 2007), conjugated microporous polymers (CMP) (Jiang et al., 2007; Li et al., 2011), covalent triazine-based frameworks (CTFs) (Kuhn et al., 2008), and porous aromatic frameworks (PAFs) (Ben et al., 2009; Peng et al., 2011; Li et al., 2018) have enriched the type of POF materials.

Ru/Carbon reported by Liang et al. shows excellent efficiency for hydrolysis of AB with high turnover frequency (TOF) value of  $429 \text{ mol (H}_2\text{) min}^{-1} \text{ mol}^{-1}$  (Liang et al., 2012). However, Ru/Carbon shows low stability indicated by recycling tests. As an outstandingly qualified catalyst, it should have excellent recyclability. Normally, the issue of the aggregation of catalysts or the exfoliation of catalysts is the decisive factor. In this paper, we present the design and synthesis of PAF-72 with small pore size and N-decorated skeleton, which is employed as a scaffold to anchor Ru for hydrolysis AB under mild conditions. 9,10-dicyanoanthracene (DCA) containing nitrile group was used as a building unit to construct PAF material (PAF-72) *via* ionothermal reaction. Adequate characterizations have been carried out to confirm the structure feature and pore properties of the PAF-72. Additionally, the porous property was explored by  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  sorptions. Furthermore, we presented the Ru/PAF-72 for hydrogen generation from hydrolysis of ammonia borane (AB). Because of the N-decorated skeleton and suitable pore size, it is effective to avoid the falling off and uniting of Ru. Therefore, Ru/PAF-72 shows an excellent catalytic activity and recycling performance.

## EXPERIMENTAL

### Synthesis of PAF-72

Synthesis of PAF-72 was conducted under ionothermal condition (Figure 1A). Typically, DCA (228 mg, 1 mmol), and anhydrous  $\text{ZnCl}_2$  (136 mg, 1 mmol) were mixed and grinded in the glove box. Then the mixture was transferred into a Pyrex ampoule ( $1 \times 12 \text{ cm}$ ). The ampoule was flame-sealed under vacuum and was placed in a muffle furnace at  $400^\circ\text{C}$  for 40 h. After cooling down to room temperature, the ampoule was opened carefully and the crude product was stirred in  $\text{H}_2\text{O}$  (10 mL) and refreshed three times to remove  $\text{ZnCl}_2$ , and then washed with 1M HCl ( $3 \times 10 \text{ mL}$ ), THF ( $3 \times 10 \text{ mL}$ ), and dichloromethane (10 mL) to purify the product. Finally, the powder was dried overnight in an oven at  $100^\circ\text{C}$  to give PAF-72 as a black particle (98% yield).

### Synthesis of $\text{RuCl}_3$ and PAF-72 Mixture

PAF-72 was degassed at  $120^\circ\text{C}$  for 12 h before use.  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (10 mg) was dissolved in methanol (2 mL) and then PAF-72 (10 mg) was added into the solution. The mixture was stirred 12 h for incorporating thoroughly. After filtration, the product was wash by methanol completely to remove the  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  at surface. Finally, the powder was dried overnight in oven at  $100^\circ\text{C}$ .

### Synthesis of Ru/PAF-72 Catalysts

Ru/PAF-72 was synthesized *in situ* by reducing the  $\text{RuCl}_3$  using AB in aqueous solution.

### Catalytic Hydrolysis of AB

Catalytic testing of Ru/PAF-72 for hydrolytic dehydrogenation of AB was carried out at 298 K under atmospheric pressure. Ru/PAF-72 (10 mg) was placed in a two-necked glass container and aqueous AB solution (2 mL) was injected *via* a syringe. The mixture was mixed by using a magnetic stirrer, and the generated volume of  $\text{H}_2$  was measured by a water-filled burette. For durability tests, the reactions were repeated 10 times. The first cycle refers to the reduction of  $\text{Ru}^{3+}$  by AB and simultaneous AB hydrolysis reaction. When the hydrolysis process was completed, Ru/PAF-72 was filtered to separate from the mixture for the next cycle.

## RESULTS AND DISCUSSION

The structure was confirmed firstly by comparison of the FTIR spectra of PAF-72 and DCA. As shown in Figure 1B, the disappearance of nitrile group characteristics peak at  $2,218 \text{ cm}^{-1}$  of DCA demonstrated the successful involvement of DCA in the ionothermal reaction, and the appearance of peaks at 1,585 and  $1,203 \text{ cm}^{-1}$  indicated that the triazine ring was synthesized as desired. The XPS spectrum of Zn element showed no residual Zn element in PAF-72 (Figure S1).

Powder X-ray diffraction (PXRD) was carried out to discover the crystallinity of Figure S2. There were no intense peaks but only a broad peak which shows that PAF-72 is amorphous. This might be caused by the benzene of anthracene becoming

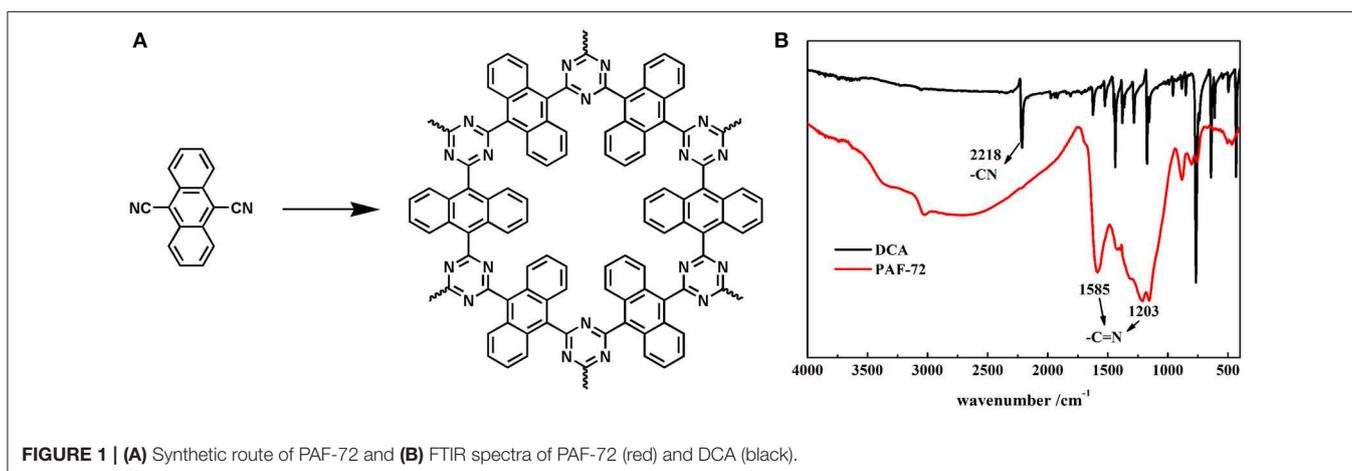
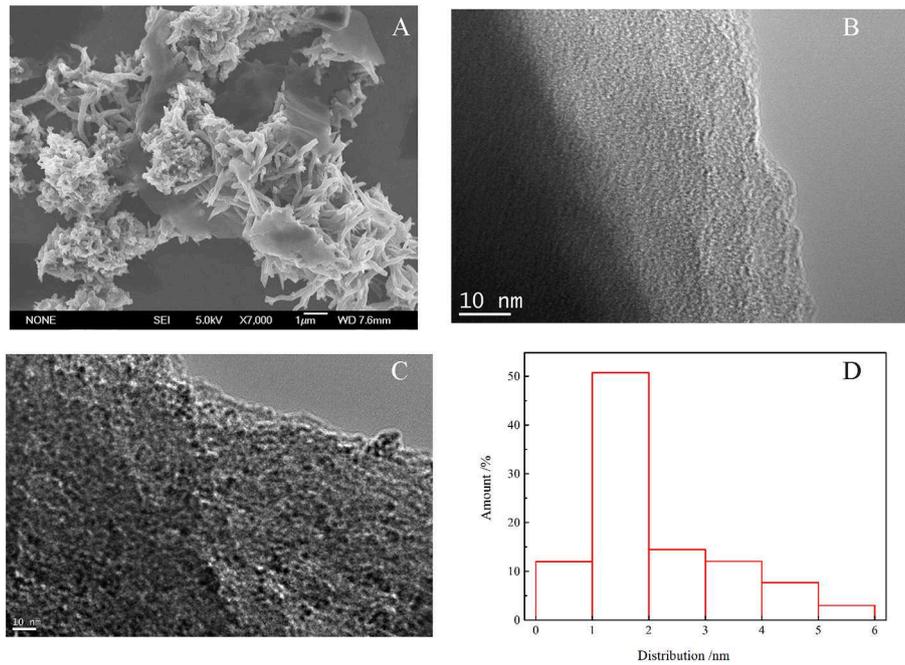
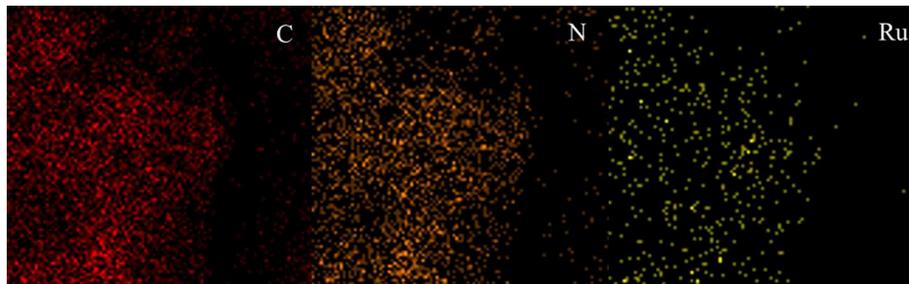


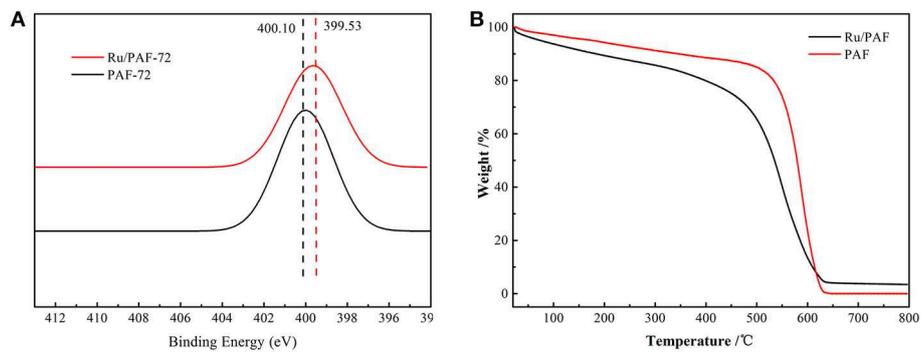
FIGURE 1 | (A) Synthetic route of PAF-72 and (B) FTIR spectra of PAF-72 (red) and DCA (black).



**FIGURE 2 | (A)** SEM of PAF-72, **(B)** TEM of PAF-72, **(C)** TEM of Ru/PAF-72, and **(D)** Ru particles diameter distribution.



**FIGURE 3 |** TEM mapping of C, N, and Ru.



**FIGURE 4 | (A)** XPS spectra (N 1s) and **(B)** TGA plots of PAF-72 and Ru/PAF-72.

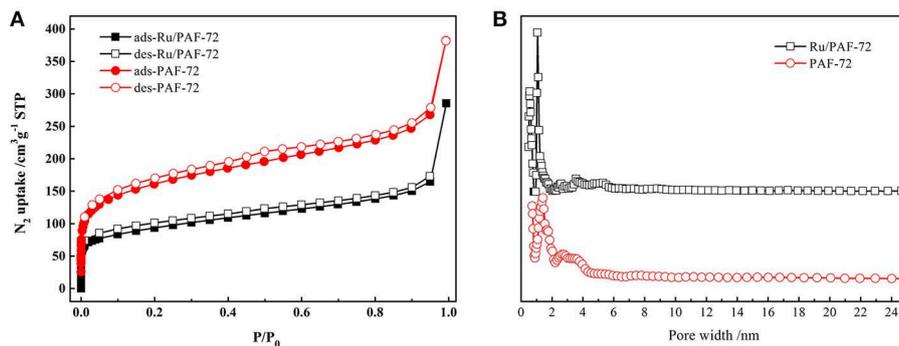


FIGURE 5 | (A) N<sub>2</sub> sorption isotherms and (B) pore width distributions of PAF-72 (red) and Ru/PAF-72 (black).

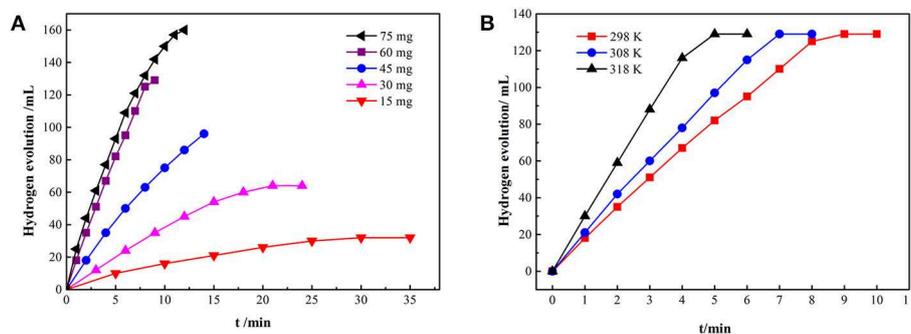


FIGURE 6 | The volume of hydrogen for the Ru/PAF-72 catalytic hydrolysis of AB with different concentrations of AB (A) and at different temperature (B).

twisted, which causes that the adjacent layers to be not completely parallel. Scanning electron microscopy (SEM) shows that the PAF-72 is in irregular blocks with nanometer dimensions (Figure 2A). Transmission electron microscopy (TEM) also indicates the amorphous texture of PAF-72 (Figure 2B). As shown in Figure 2C, the Ru nanoparticles in Ru/PAF-72 are dispersed well in the skeleton. Based on the statistics of nano measurements, the size of Ru nanoparticles is  $\sim 1\text{--}2\text{ nm}$  (Figure 2D). The image of TEM mapping also indicates that Ru is dispersed clearly (Figure 3).

The existence of Ru influences N element in the skeleton from X-ray photoelectron spectroscopy (XPS) spectrum. PAF-72 exhibits N 1s signal at 400.10 eV, which is shifted into 399.53 eV after loading Ru (Figure 4A). The Ru content in PAF-72 is 2.2 wt% via inductive coupled plasma (ICP) studies. The structure stability of PAF-72 and Ru content are also studied by thermogravimetric analysis (TGA) (Figure 4B). Because of the existence of Ru in Ru/PAF-72, there is about 3.4 wt% oxide residue, which is corresponding to 2.58 wt% Ru.

The porosities of PAF-72 and Ru/PAF-72 were studied by N<sub>2</sub> sorption measurement at 77 K (Figure 5A). At low relative pressure, there is a sharp increase for both PAF-72 and Ru/PAF-72, indicating that they are microporous textures. At high relative pressure, a steady linear increase is observed. Calculated from the Brunauer-Emmett-Teller (BET) model, the apparent surface area

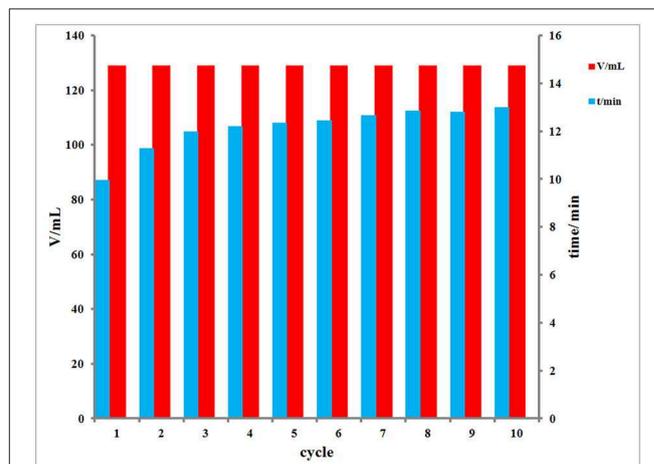


FIGURE 7 | The volume and time for the Ru/PAF-72 catalytic hydrolysis of AB from 1st to 10th cycles at 298 K.

of PAF-72 is  $582\text{ m}^2\text{ g}^{-1}$ . The pore size distribution is calculated from nonlocal density functional theory (NLDFT). It gives two narrow peaks at 0.7 and 1.4 nm (Figure 5B). In addition, CO<sub>2</sub> and CH<sub>4</sub> sorptions of PAF-72 at 273 and 298 K were measured (Figures S3–S8). The CO<sub>2</sub> uptake at 273 and 298 K is 36.9 and

25.2 cm<sup>3</sup>·g<sup>-1</sup>, respectively (Figure S3). The BET surface area of Ru/PAF-72 is 332 m<sup>2</sup> g<sup>-1</sup> and the pore width converges at 0.5 and 1.1 nm. The decrease of BET surface area and pore width indicate that pore volume is occupied by Ru nanoparticles.

The hydrolysis of AB was tested after Ru was proved to be loaded into PAF-72. Firstly, at 298 K, different amount of AB is used for hydrolysis to confirm the best concentration of AB after recording the hydrolysis and calculating the TOF (Figure 6A). With the increase concentration of AB, the reaction speed enhances, and the maximum TOF is 294 mol (H<sub>2</sub>) min<sup>-1</sup> mol<sup>-1</sup> (Ru) when the amount of AB is 60 mg (Table S1). Besides, the temperature can also influence the reaction speed. The total hydrolysis time decreased with the increase of reaction temperature (Figure 6B). Furthermore, Ru/PAF-72 shows very excellent stable and continuous catalytic ability even after 10th cyclic measurement (Figure 7). By comparison, carbon black loaded Ru material shows great performance during the first hydrolytic process, but during the fourth time the total hydrolysis time increases, clearly indicating that carbon black is not a good scaffold to anchor metal (Figure S9).

In summary, PAF-72 was synthesized successfully *via* ionothermal reaction. The properties of PAF-72 were well-investigated and the porosity was explored by N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> sorptions. Furthermore, Ru/PAF-72 exhibits favorable catalytic abilities for hydrolyzing AB. Such a POF material containing a nitrogen skeleton promises great potential as a scaffold for metal catalysts.

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## DATA AVAILABILITY

All datasets generated for this study are included in the manuscript/Supplementary Files.

## AUTHOR CONTRIBUTIONS

GZ and HR conceived the idea, designed, and supervised the experiment. PC designed and carried out the experiments and performed the data interpretation. PC and HR drafted the manuscript. All authors contributed to the writing of the manuscript.

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## SUPPLEMENTARY MATERIAL

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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