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1 2		
3 4	1	View Article Online Ruthenium nanoparticles supported on nitrogen doped porous carbon as a highly efficient 39/C8NJ06296J
5 6	2	catalyst for hydrogen evolution from ammonia borane
7 8	3	
9 10	4	Zhenkai Cui, Yueping Guo, Zhishang Feng, Dan Xu, Jiantai Ma*
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Serie Sty	11	
	12	
327	13	Abstract
	14	As one of the cleanest energies in future, hydrogen is extensively studied for its production and
30 1 30 1 30 1	15	storage. In this work, we prepared a nitrogen-doped porous carbon material (NC-Fe) via the facile
ନ୍ଧ ଅ ଅ ଅ	16	pyrolysis of a porous organic polymer (POP). The as-prepared NC-Fe material was then modified
of Annu Annu Annu Annu Annu Annu Annu Ann	17	with small ruthenium nanoparticles (Ru NPs), obtaining the Ru/NC-Fe catalyst for efficiently
ାଞ୍ଚି6 ୧୦୦ ଅ	18	catalytic hydrogen generation from ammonia borane (AB). The prepared catalyst was detailed
abed 8	19	characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission
<u>쿜</u> 0 41	20	electron microscope (TEM), nitrogen absorption-desorption measurements and X-ray photoelectron
42 43	21	spectroscopy (XPS). The small Ru NPs were highly grafted on the surface of NC-Fe support. In the
44 45	22	catalytic hydrolysis of AB, the Ru/NC-Fe catalyst shows superior catalytic activity with high
46 47	23	turnover frequency of 102.9 $mol_{H2} min^{-1} mol_{Ru}^{-1}$ and low activation energy of 47.42 kJ mol ⁻¹ as
48 49	24	compared with many other reported catalysts. This mainly attributed to the highly dispersed Ru NPs
50 51	25	on the NC-Fe surface, which provided abundant accessible active sites. Furthermore, the Ru/NC-Fe
52 53	26	catalyst also exhibits excellent magnetically recyclability and can be reused for at least five cycles.
54 55	27	Thus, this work provided a useful strategy for fabrication of POPs material derived catalysts for
56 57	28	various catalysis applications.
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60	30	

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1 Introduction:

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To solve the increasingly serious energy crisis, developing clean renewable energy is believed to be an effective way. Hydrogen, due to its advantages such as high energy density, non-toxicity, and easy storage, has been regarded as a potential feasible renewable energy.¹ Among the studied hydrogen storage materials, ammonia borane (AB) has received extensive attention from researchers due to its high hydrogen storage capacity (19.6 wt %).² Hydrogen can be released efficiently and safely from the hydrolytic dehydrogenation of AB in the presence of suitable catalysts according to the following eqn (1)

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$$H_3NBH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2$$
(1)

Studies on catalytic hydrogen generation from AB have also been reported in recent years.³⁻⁵ Especially, these studies mainly focus on the development of catalyst system in the AB-based hydrogen generation system,^{6,7} including studies on catalyst active sites and catalyst supporting materials. In studies on catalyst active sites, precious metals, such as Pt,⁸ Au⁹ and Ag¹⁰ have an ultrahigh activity. However, the high prices and low reserves hindered their large-scale application. In contrast, Ru, as a cheap and efficient catalyst for AB hydrolysis, attracted great interest of researchers.¹¹⁻¹⁵

17 Due to the size effect, noble metal nanoparticles can very easily agglomerate during catalytic process. Therefore, to reduce the consumption of precious metal active sites and the leaching in the reaction, 18 these catalysts are generally loaded on supporting materials during preparation.^{16,17} For effectively 19 20 controlling the loading form of catalyst active sites, usually the adsorption-reduction method is adopted to fabricate the catalysts.^{18,19} In hydrogen generation, researchers also try to increase the 21 hydrogen generation efficiency of the catalysts by loading them on different types of carriers. For 22 instance, Fan et al. dispersed Ru nanoparticles on carbon, nanodiamond and nanoclusters, the 23 obtained catalysts with high catalytic activity toward hydrogen generation from AB hydrolysis.²⁰⁻²² 24 25 Xiong et al. loaded RuCuNi alloy on CNTs, while Luo et al. loaded Ru on MIL-101 to improve the 26 effect of application of catalyst and increase the hydrogen generation efficiency of AB hydrolysis.23,24 27

Porous organic polymers (POPs), as an emerging type of catalyst supporting materials, have
 attracted a lot of attention due to their structural adjustability, structural diversity, fine stability and
 other characteristics during structural construction.^{25,26} Beside satisfactory studies in the fields of

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supercapacitors,²⁷ gas absorption and separation,^{28,29} and organic cells,^{30,31} they have also seem/C8NJ06296J
desirable effects in the field of catalysis.^{32,33} In addition, many POPs materials were prepared using
nitrogen-containing precursors, thus can be further pyrolyzed to fabricate nitrogen-doped carbon
materials (NC), and further serve as ideal catalyst supports to expand the scope of application of
such materials.³⁴⁻³⁶

Based on the above progresses in hydrogen production materials, this work prepared a POP material using the ferrocenecarboxaldehyde and melamine as the starting material. The obtained POPs material has adjustable channel.³⁷ NC-Fe material was prepared via the pyrolysis of the obtained POP material, and Ru NPs were loaded on the NC-Fe as active sites. The ferrocenecarboxaldehyde formed iron oxide exhibits magnetical property, thus the catalysts can be separated from the reaction solution using an external magnet. The prepared Ru/NC-Fe catalyst was used in the catalyze hydrogen generation from AB hydrolysis, and shows excellent catalytic activity as compared with many other noble metal-based catalysts. This study may promote the research of fabrication POPs derived supported catalysts for various catalysis applications.

16 Experimental

17 Synthesis of NC-Fe

The supporting material NC-Fe used in this study was obtained through heat treatment of a porous organic polymer of POP structure. More specifically, the synthesis of POP is conducted according to a previous work.³⁸ In the specific experimental process, ferrocenecarboxaldehyde (6 mmol, 1.226 g) and melamine (4 mmol, 504 mg) were added to a 100 mL flask, and 20 mL dimethyl sulfoxide was added as the reaction solvent after stirring and condensation. After nitrogen degassing, the reaction was sustained for 40 h at 180 °C and resulted in a black colloid, which was filtered and washed using methanol, N, N-Dimethylformamide and Tetrahydrofuran. The product was dried for 12 h at 120 °C to obtain black POP powder. The acquired POP powder was calcined for 2 h at 700 °C at the heating rate of 2 °C min⁻¹ under N₂ protection to obtain the NC-Fe carrier.

27 Synthesis of Ru/NC-Fe

The Ru/NC-Fe catalyst was prepared according to the adsorption-reduction method. Typically, 300
mg NC-Fe carrier was ultrasonically dispersed in 100 mL H₂O, and then, 38.8 mg RuCl₃•3H₂O was
dissolved in H₂O. After that, this aqueous solution was added to the dispersed solution of NC-Fe,

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and the mixture was stirred for 24 h. Under ice bath conditions, the aqueous solution containing 280/C8NJ06296J
 mg NaBH₄ was added, followed by stirring for 4 h to obtain Ru/NC-Fe catalyst.

Catalytic performance and stability test

In the hydrogen generation process, 4 mg Ru/NC-Fe catalyst was added to 5 mL water for uniform ultrasonic dispersion. Then, AB was dissolved in water with the successive doses of 2 mg, 4 mg, 6 mg and 8 mg to obtain AB aqueous solutions of different concentrations. After that, the two solutions were mixed, and the drainage method was adopted at 25 °C to measure and record the volume of generated hydrogen.³⁹ The turnover frequency (TOF, units of $mol_{H2} min^{-1} mol_{Ru}^{-1}$) of the generated hydrogen could be calculated using eqn (2). In the cycling experiment, an equal volume of AB aqueous solution was added after completion of each reaction to sustain the system reaction, so that the hydrogen generation rate could be measured.

$$TOF = \frac{V_{H_2}}{22.4 V_S C_{R_u} t}$$
(2)

13 Where V_{H2} was the volume of the hydrogen, V_s was the solution volume (5mL in this report), C_{Ru} 14 was the Ru concentration, and t was the reaction time.

In a typical experiment, we introduced the POPs and NC-Fe into the AB aqueous solutions, there are no hydrogen bubbles were monitored. And hydrolysis reaction was triggered immediately when the Ru/NC-Fe was introduced into the reactor, which indicating that Ru species were the active sites for AB hydrolysis.

19 Catalyst characterization

The structure and crystallinity of the catalysts were measured by the Powder X-ray diffractometer (XRD, Rigaku D/max-2400), Cu-Ka radiation source was used and the scan range 20 from 20° to 80°. The electronic states of the catalysts were measured by X-ray photoelectron spectroscopy (XPS, PHI-5702), and the binding energies were calibrated use the C1s peak at 284.8 eV. The morphology of the catalysts observed by scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F30,200 kV), the TEM diffraction pattern verified the structure of the catalysts. Inductively coupling plasma atomic emission spectrometer (ICP-AES, PQ 9000) was used to determine the metal loading of the as-prepared catalyst. Fourier transform infrared spectrometer (FT-IR) and thermogravimetric analysis (TGA, TA-Q50) was also employed to analyze the prepared catalyst. Specific surface areas of the catalysts were obtained by



Results and discussion



Scheme 1 Synthetic route of the Ru/NC-Fe nanocatalyst.

9 Characterization of Ru/NC-Fe nanocatalyst

Scheme 1 shows the synthetic route of the Ru/NC-Fe nanocatalyst. The ferrocenecarboxaldehyde and melamine was used as precursor, the two-dimensional (2D) nanosheets materials (CN) and γ -Fe₂O₃ nanoparticles formed during the heat treatment. Due to the lone pairs of electrons which form the rich nitrogen atoms in NC-Fe, the Ru³⁺ can be adsorbed on the surface of NC-Fe equably. Finally, the Ru/NC-Fe nanocatalyst formed when the solution containing NaBH₄ was added.

To understand the structure of the synthesized POP, the XRD results of the NC-Fe carrier acquired through heat treatment at 700 °C and the Ru/NC-Fe catalyst were analyzed. As can be seen in Fig. 1a, before further processing, the synthesized POP material had an amorphous structure. Firstly, the Fe in the POP structure crystallized and generated crystalline compounds after heat treatment and carbonization at 700 °C. The peaks observed at 30.3, 35.7, 43.4, 53.9, 57.4 and 63.0° correspond to the crystalline faces of (220), (311), (400), (422), (551) and (440), respectively, and this is consistent with the crystalline phase of γ -Fe₂O₃ (PDF#39-1346). ⁴⁰ Then, the Ru peak could be detected after

view Article Online active site loading. Further, the Fourier transform infrared (FTIR) spectrum of the synthesized POP/C8NJ06296J the NC-Fe carrier and the Ru/NC-Fe catalyst also suggested the crystallization of Fe (Fig. 1b). The peaks at 700–550 cm⁻¹ are due to the multiple Fe-O stretching mode of γ -Fe₂O₃.⁴¹ Initially, the peaks corresponded to the bonding of ferrocene in the raw material appeared at 490 cm⁻¹, 1103 cm⁻¹ and 807 cm^{-1} and the C=C at 1558cm⁻¹, respectively. After the carbonization, these characteristic bands almost disappeared as the result of Fe crystallization. Besides, after the carbonization, the peak positions at 3396 cm⁻¹ and 2924 cm⁻¹ remained unchanged, while the N-H band at 1190 cm⁻¹ moved towards the low-frequency direction, possibly because of the degradation of aminal, as reported by Zhou et al..³⁷



Fig. 1 XRD patterns (a) and FT-IR spectra (b) of POP, NC-Fe and Ru/NC-Fe.

In accordance with the above conclusion, the electron diffraction pattern (Fig. 2a) also indicated an amorphous structure of the synthesized POP material. According to the Fig. 2b the size of POPs particles were about 30nm. After the heat treatment, the large dark spots were Fe oxides (Fig. 2c), and the diffraction spots, mainly because of the polycrystal with relatively large grains formed by Fe.⁴² After metal Ru NPs loading, the small dark spots were observed (Fig. 2f), which were Ru NPs with an average pore size of $3 \sim 4$ nm. In the electron diffraction pattern (Fig. 2e), there were broadened diffraction rings, suggesting that the loaded metal had formed polycrystalline compounds, and which were composed of nanocrystals in very small particles. As shown in Fig. 2g, the loaded Ru active sites were uniformly distributed on the surface of NC-Fe carrier, forming uniform active sites, which would facilitate the catalytic reaction.

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Fig. 2 TEM image and HRTEM image of as-prepared POP, NC-Fe and Ru/NC-Fe (a)-(f). HAADF-STEM (high-angle annular dark field scanning transmissionelectron microscopy) image and elemental mapping images (g).

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Fig. 3 XPS survey spectra of wide-scan spectrum of Ru/NC-Fe catalyst (a), Ru $3p_{3/2}$ scan spectra (b), N 1s scan spectra (c) and Fe 2p scan spectra (d).

The XPS spectra of the obtained Ru/NC-Fe catalyst showed that the catalyst mainly consisted of C, Ru, N and Fe elements (Fig. 3a). In Fig. 3b, the peaks at Ru $2p_{3/2}$ (462.25 eV) and Ru $2p_{3/2}$ (464.7 eV) could be assigned to metallic ruthenium (73.4%) and ruthenium oxide (26.6%),⁴³ indicated that Ru NPs was mainly present in the form of Ru (0). In Fig. 3c, the peak at 397.7 eV, 399.6 eV, 401.9 eV and 404.7 eV could be assigned to pyridinic-N (59.4%), pyrrolic-N (4.9%), graphitic-N (9.1%), and oxidized-N (26.6%) respectively in N 1s scope.^{37,44,45} The pyridinic nitrogen and pyrrolic nitrogen atoms can coordinate with Fe to form Fe-Nx active site and facilitate the catalysis. The peak at 709.2 eV could be assigned to Fe 2p_{3/2}, while the peak at 724.0 eV could be attributed to Fe $2p_{1/2}$, the two statellite peaks are important characteristic features of γ -Fe₂O₃ phase (Fig. 3d).⁴⁶

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Fig. 4 Nitrogen adsorption-desorption isotherm and BJH pore size distribution of as-prepared POP, NC-Fe and Ru/NC-Fe (a), TGA curves of as-prepared POP (b).

The nitrogen adsorption-desorption isotherms showed the corresponding pore size distribution curves of as-prepared POP, NC-Fe and Ru/NC-Fe. As can be seen from Fig. 4a, when $P/P_0 > 0.4$, the curve obtained was a Type-IV isotherm, suggesting that the obtained catalyst material had a mesoporous structure.⁴² The BET value and the average pore width of the as-prepared POP, NC-Fe and Ru/NC-Fe were as-prepared POP (324.8 m² g⁻¹, 46.3 nm), NC-Fe (469.9 m² g⁻¹, 30.6 nm) and Ru/NC-Fe (278.8 m² g⁻¹, 30.5 nm). Compare with the POP and NC-Fe, the reduction of major peak center suggested the formation of porous structure and the increased of BET value suggested the formation of small Fe-based nanoparticles during sintering. The pore width decreased slightly after loaded the Ru NPs on the NC-Fe, it means most of the loaded Ru NPs enter the channel structure. The size of channel restricted the growth of Ru and got the small catalyst particles, the lone pairs of electrons anchored the Ru NPs on NC-Fe firmly. The fine Ru(0) active sites distributed on the NC-Fe surface increased the rate of hydrogen generation. According to the TGA curves of as-prepared POP (Fig. 4b), there was a very significant weight loss at 250-700 °C, mainly because of the volatilization of nitrogen-containing gas during the formation of NC nanosheets in the carbonization process. Above 700 °C, no obvious weight loss was observed, and therefore, 700 °C was selected as the carbonization temperature. Besides, the sintering process of the POPs carrier could increase the stability of channel, improve the thermal stability, create more stable NC-Fe carrier and make such catalyst carriers more applicable to industrial applications.

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Catalytic hydrogen production

The prepared Ru/NC-Fe catalyst was used in the catalytic hydrogen generation from AB. The hydrogen generation volume using Ru/NC-Fe catalyst at different AB concentrations in the reaction system were shown in Fig. 5a. With the increased AB concentration in the system, the total volume of hydrogen generation increased. The straight line in Fig. 5a (insert) with a slop of 0.0861 (close to zero) indicates the influence of AB concentration on hydrogen generation rate was extremely insignificant. It suggesting that the reaction is a zero order with respect to the AB concentration for hydrolysis of AB, and the reaction within this range of concentration was controlled by the active sites.

The influence of the Ru/NC-Fe catalyst dosage on hydrogen generation was studied as shown in Fig. 5b. Clearly, with the increased catalyst dosages, hydrogen generation rates increased. When the amount of catalyst reached 5 mg, hydrogen generation rate reached its maximum. However, when the active sites reached a certain concentration, catalyst particles would agglomerate, giving rise to the non-uniform dispersion of active sites, and thus, reducing the hydrogen generation rate. In further studies, 4 mg of the catalyst was chosen to achieve a more stable hydrogen generation process. Calculated based upon the Ru loading capacity of 4.752 wt % (ICP results), the maximum TOF was 102.9 $mol_{H2} min^{-1} mol_{Ru}^{-1}$. The comparison of TOF with previous studies was showed in Table 1. The Ru/NC-Fe catalyst in this wok shows a higher activity and lower activation energy in the catalytic hydrogen generation from AB, probably due to the highly dispersed small Ru NPs on the surface of NC-Fe, which could provide much more active sites in the catalytic process.

1 2	Table 1 Comparison o catalysts for dehydrog
	catalyst
	Ru@Co/C black
	Ru@Co/graphene
	Ru@Al ₂ O ₃
	PtPd NPs
	PtNi@SiO ₂
	Pt-CoCu@SiO ₂
	Pt/C (2 wt%)
	Ru/NC-Fe
3	
	(a)
	3.0 -
	E 25
	0 1.5-
	CH 1.0
	e 0.5 -
	0.0
4	⁰ 1 ² Tin

of TOF values and activation energy with the recently reported heterogeneous/C8NJ06296J enation of AB.

catalyst	T/°C	$TOF/mol_{H2}min^{-1}mol_{M}^{-1}$	Activation energy/kJ mol ⁻¹	Ref.
Ru@Co/C black		29.1	21.2	47
Ru@Co/graphene		40.5	-	48
Ru@Al ₂ O ₃		83.3	48	49
PtPd NPs	25	22.51	57.3	50
PtNi@SiO ₂	30	20.7	54.76	51
Pt-CoCu@SiO ₂	30	272.8	51.01	52
Pt/C (2 wt%)	25	111	62	53
Ru/NC-Fe	25	102.9	47.42	This study

Fig. 6 Effect of different temperature on hydrogen generation (a). The Arrhenius plot of the hydrogen generation rates (b).

The hydrogen generation volumes using Ru/NC-Fe catalyst at different temperatures of 25, 30, 35, 40 and 45 °C were shown in Fig. 6a. With the increased temperature, the rate of AB hydrolysis significantly increased. When the system temperature was 25 °C, the reaction ended after 280 s. However, when the system temperature was 45 °C, the reaction ended within 90 s. The activation energy (E_a) of the reaction system was estimated using Arrhenius law (Fig. 6b):

$$\operatorname{Ln} r = \ln k_0 - \frac{E_a}{RT}$$
(3)

Where r was the rate of the reaction $(mL_{H2} \text{ min}^{-1} \cdot \mathbf{g}_{Ru}^{-1})$, k_0 was the rate constant $(mL_{H2} \text{ min}^{-1} \cdot \mathbf{g}_{Ru}^{-1})$ ¹), E_a was the activation energy, R was the gas constant [8.3143 kJ (mol•K)⁻¹], T was the reaction temperature (K).

Comparing the results with those reports adopted the same system (Table 1), the E_a of R@/NC1F@/C8NJ06296J
catalyst was lower than that of the Pt and Ru catalysts at different kinds of carriers. Possibly, the
channel of the NC-Fe carrier was beneficial for the passage of AB molecules and products in the
solution, which promoted the progress of reaction.

Fig.7 Durability test (a) and the hysteresis curve of the NC-Fe and Ru/NC-Fe catalysts (b).

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Fig. 7a shows the cycle performance of Ru/NC-Fe catalyst. It can be seen that, after five cycles, it took 80 mins for the system to complete the reaction. And according to the insert Fig. 7a, the total generated hydrogen was almost unchanged. Fig. 7b showed the hysteresis curve of the NC-Fe and Ru/NC-Fe catalysts. The M_s was 6.35 emu g^{-1} in NC-Fe catalysts and 1.57emu g^{-1} in Ru/NC-Fe catalysts. The H_c was 297.33 Oe in NC-Fe catalysts and 320.9 Oe in Ru/NC-Fe catalysts. It means the catalysts contains γ -Fe₂O₃, and the catalysts can recycle through the strong magnet easily, see the insert Fig.7b. The slightly reduced hydrogen generation activity of the catalyst could be explained mainly by two reasons. Firstly, the by-product metaborate generated in the reaction process was attached to the Ru NPs, covering the active sites, and leading to a decline in activity.⁵⁴ Secondly, due to the agglomeration of catalyst, active sites overlapped with each other, and there were insufficient electron sites for the reactants, which resulted in the decline of hydrogen generation rate. In addition, the increase of reactant viscosity resulted in low dispersion of AB also contributed to the decline of reaction activity.55

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1	Conclusion DOI: 10.1039/C8NJ06296J
2	In summary, this work obtained a mesoporous NC-Fe material through the carbonization of a
3	ferrocenecarboxaldehyde-based POP material, and the obtained NC-Fe was then modified with
4	highly dispersed Ru NPs to form the Ru/NC-Fe catalyst. The Ru/NC-Fe catalyst was used in the
5	catalytic hydrogen generation from ammonia borane, and showed excellent catalytic activity as
6	compared with many other noble metal-based catalysts. The reason should be due to the highly
7	dispersed Ru NPs on the NC-Fe surface, which provided abundant accessible active sites for the
8	catalytic process. Moreover, the prepared catalyst can be magnetically recovered and recycled due
9	to its ferromagnetism. Therefore, the Ru/NC-Fe catalyst proposed in this paper provides a useful
10	platform for constructing POPs derived catalyst supported various metal catalysts with highly active
11	sites dispersion in various catalytic the applications.
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