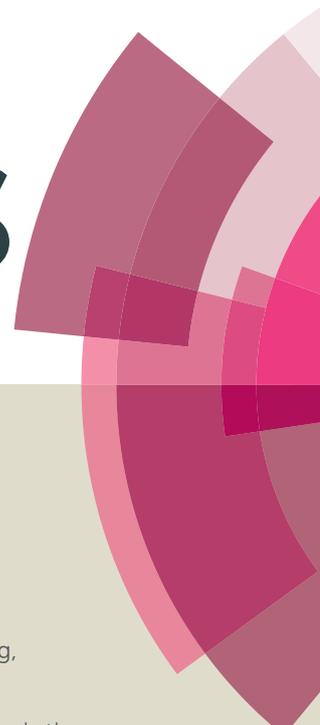


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- Effects of nitrogen-dopants on Ru-supported catalysts for acetylene hydrochlorination

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1 Abstract

2 A series of N-doped spherical active carbon were synthesized via the pyrolysis of
3 melamine in activated carbon, and used as the support to prepare Ru-based catalysts for
4 acetylene hydrochlorination reaction. The catalytic performance assessments indicate that
5 the N-doped carbon support can increase greatly the activity and the stability of Ru-based
6 catalysts. The optimal activity is achieved over Ru/SAC-N700, with the acetylene
7 conversion of 99.8% under the conditions of 170 °C, C₂H₂ gas hour space velocity
8 (GHSV) of 180 h⁻¹, the feed volume ratio of V(HCl)/V(C₂H₂) of 1.1 after 30 h. Using
9 characterizations of BET, FT-IR, XPS, TPR, TPD, TG, etc., it is illustrated that N-dopants
10 can increase the dispersion of Ru elements, enhance the adsorption of reactants and the
11 desorption of the product, and reduce significantly the coke deposition, consequently
12 resulting in higher catalytic activity of Ru/SAC-N700. It is suggested that the
13 pyridine-nitrogen plays an important role in augment of catalytic activity of Ru-supported
14 catalysts.

15 **Keywords:** acetylene hydrochlorination, N-doped carbon, Ru catalysts

16 1. Introduction

17 Acetylene hydrochlorination reaction is the dominant pathway to produce vinyl
18 chloride monomer (VCM) in polyvinyl chloride (PVC) industry of China, which
19 currently utilizes carbon-supported HgCl₂ as the catalyst. However, mercuric chloride is
20 highly toxicity and tends to sublime, resulting in the severe environmental pollution
21 problems.¹ In 2013, more than 140 countries signed "the Minamata Convention on
22 Mercury" so as to inhibit the trade and application of mercury over the world.² Hence, it
23 is urgent to explore environmental-benign non-mercury catalysts for acetylene

24 hydrochlorination.

25 Non-mercuric noble metallic catalysts, involving Au,³⁻⁸ Pd,⁹ Pt,^{10, 11} etc., have been
26 studied for the acetylene hydrochlorination, following the pioneer work of Hutchings¹² on
27 Au catalysts. Taking into account the cost of the catalyst, the Ru-based catalyst is
28 considered as a promising candidate for the non-mercury catalyst of acetylene
29 hydrochlorination.¹³⁻¹⁸ For instance, the bimetallic Ru1Co3/SAC catalyst showed an
30 acetylene conversion of 95% after 48 h under the condition of 170 °C and C₂H₂ GHSV of
31 180 h⁻¹.¹⁷ The Cu-Ru catalyst supported on carbon nanotubes (Cu400Ru/MWCNTs)
32 showed an acetylene conversion of 51.6% at the conditions of 180 °C, V(HCl)/V(C₂H₂) =
33 1.2 and GHSV(C₂H₂) = 180 h⁻¹.¹⁶ However, it is essential to improve further the catalytic
34 activity for ruthenium-based catalysts, so as to develop an efficient non-mercury catalyst
35 for acetylene hydrochlorination in the view of industrial application.

36 Heteroatom-doped carbon materials have shown promising properties to prepare
37 electrodes in supercapacitors¹⁹, electrocatalysts for the oxygen reduction reaction (ORR)
38 in fuel cells.^{20,21} and cathode materials for lithium ion batteries,^{22, 23} etc. In particular,
39 Bao and coworkers²⁴ prepared a nanocomposite of nitrogen-doped carbon, which showed
40 catalytic activity for acetylene hydrochlorination, with the acetylene conversion of 80%
41 at 200 °C and a space velocity of 30 h⁻¹. Dai et al.²⁵ prepared B, N-doped graphene
42 catalysts, which showed the initial acetylene conversion about 95% under the conditions
43 of 150 °C, C₂H₂ GHSV of 36 h⁻¹. Zhou et al.²⁶ reported a Cu-based catalyst supported
44 N-doped carbon nanotubes, showing the initial acetylene conversion about 45.8% under
45 the conditions of 180 °C and C₂H₂ GHSV of 180 h⁻¹. Recently, Zhao et al. reported that
46 the N-doped carbon support can increase the activity of Ru-based catalysts for the

47 reaction of acetylene and 1, 2-dichloroethane (EDC) at 250 °C and total liquid hourly
48 space velocity of EDC 0.2 h⁻¹.²⁷ Therefore, we are inspired to study the effect of N-doped
49 carbon supports on the activity of Ru-based catalysts for acetylene hydrochlorination.

50 In this article, we prepared a series of Ru-based catalysts with the support of
51 N-doped spherical active carbon synthesized via the pyrolysis of melamine in activated
52 carbon, and assessed the catalytic activity for acetylene hydrochlorination. The results
53 show that with the N-doped carbon support, the activity and the stability of Ru-based
54 catalysts are increased greatly. The influence of N-dopant on the structural, adsorption
55 properties and active species of Ru-based catalysts were characterized by BET, FT-IR,
56 XPS, TPR, TPD, TG, etc.

57 **2. Experimental**

58 **2.1 Catalyst preparation**

59 In a typical experiment, the pitch-based spherical activated carbon (SAC, 10 g,
60 20–40 mesh) was mixed with melamine (5 g) in deionized water (50 mL) at 343 K under
61 stirring for 18 h. After filtration, the mixture was dried at 393 K overnight under vacuum,
62 and then experienced the carbonization at the temperature of 600, 700 or 800 °C for 1 h
63 in a quartz tube under N₂ atmosphere at a flow of 100 cm³ min⁻¹ with a heating rate of 10
64 K min⁻¹. The obtained N-doped carbon samples were denoted as SAC-N600, SAC-N700
65 and SAC-N800, respectively.

66 The Ru-based catalysts (Ru/SAC-N) were prepared via a wetness impregnation
67 technique using the N-doped carbon as the support. A solution of RuCl₃ (209.5 mg) in
68 deionized water (12 mL) was added dropwise to the N-doped carbon (10 g) under stirring
69 at room temperature, followed by aging at 60 °C for 12 h. The product was then dried at

70 150 °C for 12 h and then assessed the catalytic performance for acetylene
71 hydrochlorination. The obtained samples were denoted as Ru/SAC-N600, Ru/SAC-N700
72 and Ru/SAC-N800 with the support of SAC-N600, SAC-N700 and SAC-N800,
73 respectively.

74 As a control, undoped activated carbon was also used as the support to prepare the
75 Ru-based catalyst via the similar technique, and denoted as Ru/SAC.

76 2.2 Catalyst tests

77 Catalysts were assessed in a fixed-bed stainless steel micro-reactor (i.d. of 10 mm)
78 for acetylene hydrochlorination. The temperature of the reactor was regulated by
79 CKW-1100 temperature controller produced by Chaoyang automation instrument factory
80 (Beijing, China). The pipeline was purged with nitrogen before the reaction to remove
81 water and air in the system, then acetylene (15 mL min⁻¹) and hydrogen chloride (16.5
82 mL min⁻¹) were fed through filters to remove trace impurities and via calibrated mass
83 flow controllers into the heated reactor containing the catalyst (5 mL), operated at
84 170 °C under the atmosphere pressure with a GHSV (C₂H₂) of 180 h⁻¹. The effluent from
85 the reactor was passed through a 10% sodium hydroxide aqueous solution to absorb the
86 unreacted hydrogen chloride, and then analyzed by gas chromatograph (GC-3420 by
87 Beijing Beifen-Ruili Analytical Instrument Co. Ltd.), equipped with FID detector. The
88 acetylene conversion (X_A) and the selectivity to VCM (S_{VC}) were calculated by the
89 equations (1) and (2), respectively.

$$90 X_A = \frac{\phi_{A0} - \phi_A}{\phi_{A0}} \times 100\% \quad (1)$$

$$91 S_{VC} = \frac{\phi_{VC}}{(1 - \phi_A)} \times 100\% \quad (2)$$

92 Where ϕ_{A0} = the volume fraction of acetylene in the feed and ϕ_A = the volume
93 fraction of remaining acetylene in the effluent from the reactor, respectively. ϕ_{VC} is the
94 volume fraction of vinyl chloride in the effluent from the reactor.

95 **2.3. Catalyst characterization**

96 The pore size distribution and specific surface areas of the catalysts were analyzed
97 by ASAP 2020C surface area and porosity analyzer (Micromeritics Instrument
98 Corporation, USA), degassing for 6 h at 423 K, then analyzed with liquid nitrogen
99 adsorption at 77 K.

100 The Fourier transform infrared spectroscopy (FT-IR) was performed using a Bruker
101 Vertex 70 FT-IR spectrophotometer equipped with a MCT detector at a resolution of 4
102 cm^{-1} .

103 Raman spectra were measured with Renishaw inVia reflex, with the resolution of 4
104 cm^{-1} (632.8 nm).

105 Thermogravimetric analysis (TGA) was carried out with TG-DTG simultaneous
106 thermal analyzer (NETZSCH STA 449F3 Jupiter[®], Germany) under nitrogen atmosphere
107 at a flow rate of 100 mL min^{-1} with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

108 X-ray photoelectron spectra (XPS) were recorded on a PHI-5000 Versa probe II-X
109 System. The binding energy was calibrated with respect to the C 1s level 284.80 eV of
110 aliphatic carbon.

111 Transmission electron microscopy (TEM) was conducted using a JEM2100F TEM
112 and an FEI Titan 80-300 TEM/STEM, equipped with CEOS spherical aberration
113 corrector. The samples were dispersed in ethanol and supported on carbon-film-coated
114 copper grids before the characterization of TEM.

115 Temperature-programmed reduction (TPR) experiments were performed using
116 AutoChem 2910 to determine the reduction behavior of the catalysts. For each
117 experiment, the sample was heated from 35 °C to 800 °C with a heating rate of 10 °C
118 min⁻¹. The flow gas mixture is 5% H₂/Ar with a flow rate of 20 mL/min.

119 Temperature programmed desorption (TPD) was measured by an AutoChem BET
120 TPR/TPD (Quantachrome Instruments AMI-90). The weight of the each sample was
121 fixed at 130 mg. For C₂H₂-TPD and HCl-TPD profiles, the samples were first pre-treated
122 under C₂H₂ and HCl atmosphere respectively for 4 h at reaction temperature (170 °C),
123 then pure helium was pass through the samples for 30 min and the desorption profiles
124 were recorded from 50 °C to 700 °C at a heating rate of 10 °C min⁻¹. Similarly, the
125 VCM-TPD profiles were recorded, except the pretreatment condition of VCM is at
126 100 °C for 1 h. For CO-TPD, the samples were first reduced at 400 °C for 2 h in 10%
127 H₂/Ar followed by cooling to room temperature, and then 250 uL pulse of 10% CO/Ar
128 were introduced, and the CO uptake profile was measured by a TCD detector.

129 **3. Results and discussion**

130 **3.1 N-doped carbon supports**

131 BET measurements were performed to investigate the physical structure variation of
132 carbon resulted by N-doping. Table 1 lists the specific surface area, pore volume and
133 average pore diameter of SAC, SAC-N600, SAC-N700 and SAC-N800. The N₂
134 adsorption-desorption isotherms (Fig. S1a) exhibit the type I adsorption curves,
135 corresponding to the microporous structure. The pore size distributions of N-doped
136 carbon supports are centered at 5Å according to HK model (Fig. S1b), approximate to
137 that of SAC. The N-doped carbon samples show higher surface area and total pore

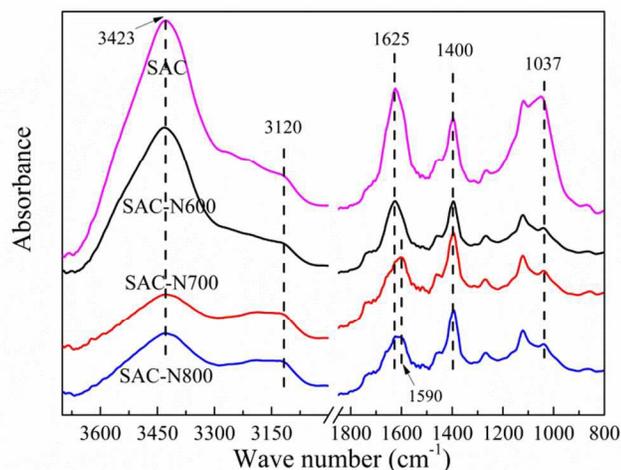
138 volume that of SAC, and SAC-N700 exhibits the highest surface area ($1325 \text{ m}^2 \text{ g}^{-1}$) and
139 total pore volume of $0.69 \text{ cm}^3 \text{ g}^{-1}$. Previously, Wang et al.²⁸ adopted ammonia to treat
140 mesoporous carbon in order to prepare the catalytic material for oxygen reduction
141 reaction, and obtained N-doped carbon with increased surface area ($2021 \text{ m}^2/\text{g}$), much
142 higher than the undoped carbon ($658 \text{ m}^2/\text{g}$). On the other hand, Saiter and coworkers²⁹
143 reported that ammonia could be generated during the decomposition of melamine at high
144 temperature. Therefore, it is reasonable to consider that the intermediate of ammonia,
145 decomposed from melamine, can etch the porous carbon so as to make the surface area
146 and the pore volume of carbon increased.

147 **Table 1** Pore structure parameters of the supports

Samples	$S_{\text{BET}} (\text{m}^2 \text{ g}^{-1})$	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore diameter (\AA)
SAC	1066	0.62	5.02
SAC-N600	1144	0.63	4.82
SAC-N700	1325	0.69	4.84
SAC-N800	1237	0.64	4.80

148
149 FT-IR spectra were measured to characterize the surface functional groups of
150 undoped and N-doped SAC. As shown in Fig. 1, SAC has major bands at 1625 cm^{-1} and
151 3423 cm^{-1} , which are respectively attributed to the C=C and O-H stretching vibrations,
152 besides the bands at 1037 cm^{-1} and 1400 cm^{-1} , which are due to the stretching of C-O and
153 the stretching vibration of the carboxyl groups.³⁰⁻³² For N-doped SAC, the intensities of
154 bands at 1037 cm^{-1} and 3423 cm^{-1} are weaker than those of SAC. For SAC-N700 and
155 SAC-N800, a small new band is observed at 1590 cm^{-1} , which is attributed to the
156 stretching of C=N groups,^{33, 34} together with another band at 3120 cm^{-1} , which is
157 attributed to the N-H and/or NH_2 groups.³⁵⁻³⁷ It is suggested that the structure of the
158 N-doped SAC consists of more nitrogen-containing functional groups and less content of

159 oxygen functional groups, comparing with undoped SAC.



160
161 **Fig. 1** FT-IR spectra of different support samples.

162
163 **Table 2** Elemental compositions on the surface of the samples determined by XPS analysis

Samples	Element composition (%)		
	C	N	O
SAC	96.2	0	3.8
SAC-N600	96.0	1.4	2.6
SAC-N700	94.8	2.0	3.2
SAC-N800	94.9	1.8	3.3

164
165 **Table 3** Relative contents and binding energies of nitrogen species of the N-doped samples

Samples	Area%, binding energy(eV)			
	N _P	N _{PYR}	N _O	N-X
SAC	-	-	-	-
SAC-N600	39.6 (398.2)	31.2 (400.0)	20.8 (401.4)	8.4 (402.7)
SAC-N700	56.9 (398.7)	8.8 (400.2)	30.9 (401.2)	3.4 (402.5)
SAC-N800	45.0 (398.4)	36.9 (400.0)	6.7 (401.4)	11.4 (402.4)

166

167 XPS spectra of different carbon samples were analyzed to distinguish the elemental
168 compositions and the species of nitrogen dopants, comparing with the undoped SAC
169 sample. As listed in Table 2, the elemental compositions of the undoped SAC sample are
170 96.2% carbon and 3.8% oxygen. While for the N-doped samples, there are nitrogen
171 component, the nitrogen content equals respectively 1.4% for SAC-N600, 2.0% for

172 SAC-N700 and 1.8% for SAC-N800. Fig. S2 displays the deconvolution of the N 1s XPS
173 spectra, indicating the existence of four kinds of nitrogen species including the
174 pyridine-nitrogen (N_P) near 398.4 eV, the pyrrole-nitrogen (N_{PYR}) at 400.1 eV, the
175 quaternary-nitrogen (N_Q) at 401.3 and the nitrogen oxides ($N-X$) near 402.5 eV. Table 3
176 lists the content of each nitrogen species in the N-doped SAC. It is clear that the
177 pyridine-nitrogen (N_P) is the dominant nitrogen species in SAC-N600, SAC-N700, and
178 SAC-N800, while the N content is dependent on the calcination temperature. The
179 SAC-N700 sample has the highest amount of pyridine-nitrogen (N_P , 56.9%) but the least
180 amount of pyrrole-nitrogen (N_{PYR} , 8.8%).

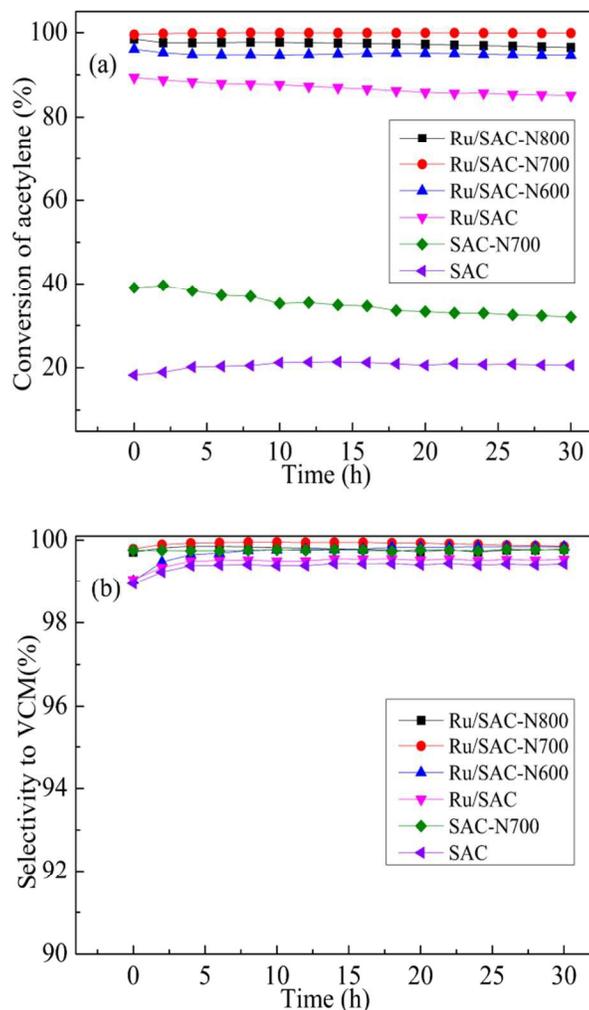
181 Previously, Wong et al.³⁸ prepared the nitrogen-doped graphene (nG) via pyrolysis
182 of graphene oxide at the temperature from 400 to 1000 °C using the nitrogen-precursor of
183 melamine, and the obtained nG consisting of the quaternary N (5%), carbon nitride and
184 oxygenated N. In addition, Xia et al.³⁹ suggested that melamine molecules adsorbed onto
185 graphite oxide (GO) surfaces could be condensed into carbon nitride with increasing
186 temperature, and the removal process of oxygen species at high temperature could
187 provide active sites for nitrogen doping into graphene frameworks.

188 Saiter and coworkers²⁹ reported that ammonia could be generated during the
189 decomposition of melamine at high temperature. The possible mechanism for doping N
190 in carbon is associated with the oxygen-containing groups in the undoped SAC sample
191 (Table 2). The intermediates decomposed from melamine, including ammonia, can react
192 with the oxygen-containing groups in the SAC to make N dopants intercalated into the
193 carbon materials. It deserves to study the mechanism for N-doping in this process in our
194 future work. Table S2 lists the elemental composition of different SAC samples

195 determined by elemental analysis (Vario Micro, Elementar). It is indicated that the bulky
196 element composition of carbon samples are approximate to those determined by XPS
197 (Table 2). Therefore, the N dopants are located uniformly in the carbon supports, rather
198 than on the surface.

199 **3.2 N-doped carbon supported Ru catalysts**

200 Fig. 2 displays the catalytic performance of the supported Ru catalysts and the
201 individual supports. The SAC-N700 support shows the initial acetylene conversion of
202 39.0% and decreases to 32.0% in 30 h, much higher than those over the support SAC,
203 suggesting that N-dopants can enhance the catalytic activity of the carbon support toward
204 acetylene hydrochlorination. Over the Ru catalyst supported on SAC (Ru/SAC), the
205 initial acetylene conversion is 89.4%, reducing to 85.2% in 30 h. While using the
206 N-doped SAC as the support, the Ru catalysts display significant increase of catalytic
207 activity. The initial acetylene conversion is 96.1% over Ru/SAC-N600, 99.5% over
208 Ru/SAC-N700, and 98.5% over Ru/SAC-N800, respectively. In particular, after 30 h, the
209 acetylene conversion over Ru/SAC-N700 is 99.8%, suggesting a superior catalytic
210 stability. As for the selectivity to VCM, it is 99.5% over Ru/SAC, 99.8% over
211 Ru/SAC-N600, 99.9% over Ru/SAC-N700 and 99.8% over Ru/SAC-N800, respectively.
212 It is illustrated that N-doped SAC supports indeed improve the activity and stability of
213 the Ru catalysts.



214

215 **Fig. 2** The conversion of acetylene (a) and selectivity to VCM (b) over SAC, SAC-N700,
216 Ru/SAC, Ru/SAC-N600, Ru/SAC-N700 and Ru/SAC-N800. Reaction conditions: $T=170\text{ }^{\circ}\text{C}$,
217 $V(\text{HCl})/V(\text{C}_2\text{H}_2)=1.1:1$, $\text{GHSV}(\text{C}_2\text{H}_2)=180\text{ h}^{-1}$.

218 Table 4 lists the dispersion of Ru elements calculated on the basis of CO adsorption.
219 The dispersion is 37.5% for the Ru/SAC. For the Ru/SAC-N catalysts, the Ru dispersion
220 is higher, with the highest dispersion of 49.9% corresponding to the catalyst
221 Ru/SAC-N700, followed by Ru/SAC-N800 (49.0%) and Ru/SAC-N600 (48.2%). The
222 results illustrate that N-dopants can facilitate the dispersion of Ru nanoparticles, probably
223 due to the more defect sites caused by N dopants, which can anchor stably the active Ru

224 species.

225 **Table 4** Ru dispersion calculated according to CO uptake

Samples	CO uptake ($\mu\text{mol CO/g}$)	Ru dispersion (%)
Ru/SAC	37.1	37.5
Ru/SAC-N600	47.7	48.2
Ru/SAC-N700	49.4	49.9
Ru/SAC-N800	48.5	49.0

226

227 Fig. 3 displays the TEM images of the fresh and used catalysts. There are some
228 small black dots in the image, which are highly dispersed Ru particles on the support.
229 The average size is about 1.40 nm and 1.24 nm for the fresh Ru/SAC and fresh
230 Ru/SAC-N700 catalysts, respectively. This result indicates that the N dopants improve
231 the Ru dispersion of catalysts, which is in accord with the CO-TPD results (Table 4).
232 While for the used Ru/SAC and used Ru/SAC-N700, obvious larger black dots appear in
233 the images, suggesting somewhat aggregation or coke deposition during the reaction. The
234 average particle size of the used Ru/SAC is 2.18 nm, much larger than that of the used
235 Ru/SAC-N700 (1.63 nm), indicating that N dopants can inhibit the aggregation or coke
236 deposition during the reaction.

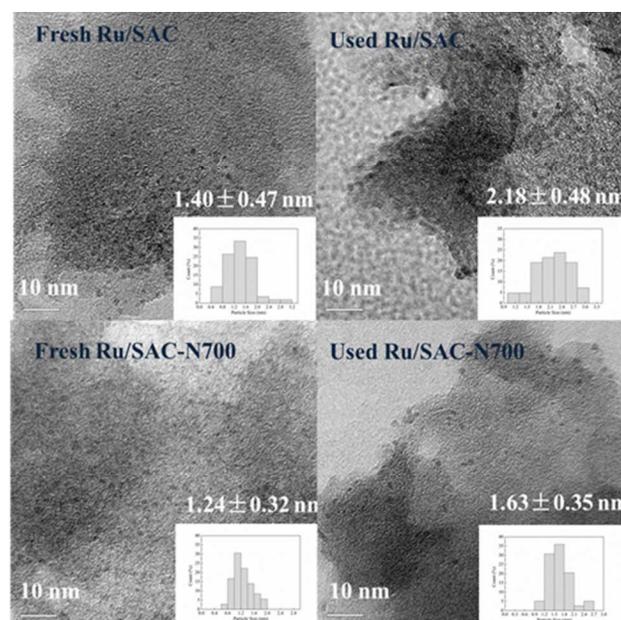


Fig. 3 TEM images of fresh and used catalysts.

237

238

239 The deconvolution of XPS Ru 3p_{3/2} spectra performed to discriminate Ru species

240 (Fig. S4 and Fig. S5). As listed in Table 5, there are four kinds of Ru species in Ru-based

241 catalysts, involving the metallic Ru (461.4 ± 0.4 eV); RuCl₃ (463.0 ± 0.3 eV); RuO₂

242 (464.5 ± 0.4 eV) and RuO_x (465.7 - 467.2 eV).⁴⁰⁻⁴² The contents of Ru species are

243 associated with the kind of support. For the fresh Ru/SAC, the dominant is RuCl₃

244 (63.0%), followed by RuO_x (16.5%) > RuO₂ (13.9%) > metallic Ru (6.6%). Whereas for

245 the Ru catalysts with the N-doped supports, the content of RuO₂ is much higher than that

246 of Ru/SAC, but the content of RuCl₃ is much lower than that of Ru/SAC. In particular,

247 the fresh Ru/SAC-N700 shows the highest content of RuO₂ (53.0%) but the lowest of

248 RuCl₃ (15.4%). After experiencing 30 h of reaction, the content of RuO₂ and RuO_x

249 decrease to some extent and the content of metallic Ru increased. It is worthwhile to note

250 that the RuO₂ species in the used Ru/SAC-N700 is still the highest.

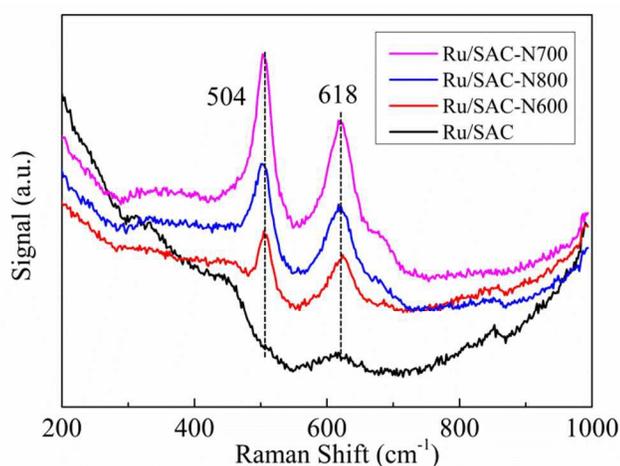
251

252 **Table 5** The relative contents and binding energies of ruthenium species in the fresh and used
253 catalysts

Samples	Area%, binding energy (eV)			
	Ru	RuCl ₃	RuO ₂	RuO _x
fresh Ru/SAC	6.6 (461.8)	63.0 (463.2)	13.9 (464.8)	16.5 (466.1)
fresh Ru/SAC-N600	10.1 (461.3)	47.1 (463.0)	28.5 (464.4)	14.3 (465.9)
fresh Ru/SAC-N700	20.6 (461.4)	15.4 (463.0)	53.0 (464.6)	11.0 (466.8)
fresh Ru/SAC-N800	13.0 (461.1)	25.3 (462.9)	29.4 (464.0)	32.3 (466.8)
used Ru/SAC	15.9 (461.7)	57.2 (463.4)	11.5 (464.8)	15.4 (466.1)
used Ru/SAC-N600	21.2 (461.6)	50.3 (463.5)	18.0 (464.3)	10.5 (466.3)
used Ru/SAC-N700	28.6 (461.6)	23.0 (463.1)	39.3 (414.5)	9.1 (466.7)
used Ru/SAC-N800	14.2 (461.4)	29.6 (463.2)	27.8 (464.9)	28.4 (466.3)

254

255 Moreover, Raman spectra were measured to confirm the existence of RuO₂. As
256 shown in Fig. 4, for the Ru catalysts with the N-doped supports, there are two sharp
257 bands at 504 and 618 cm⁻¹ corresponding to the species of RuO₂,⁴³ and the band intensity
258 increases in the order of Ru/SAC-N600 < Ru/SAC-N800 < Ru/SAC-N700. In contrast, for
259 the catalyst Ru/SAC, the bands due to RuO₂ are relative small. It is illustrated that the
260 N-doped supports can greatly increase the amount of the component RuO₂ in Ru catalysts,
261 in accord with the results in Table 5.



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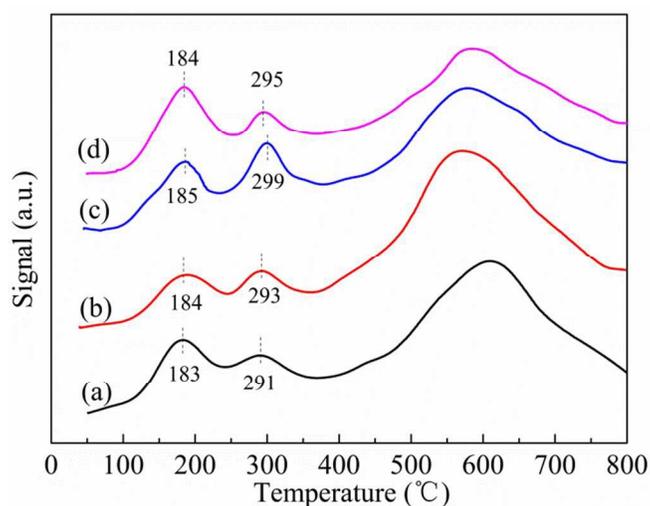
Fig. 4 Raman spectra of the fresh catalysts

264

265

According to our previous work, the pyridinic N-doped graphene support is
beneficial to enhance electron transfers between the support and the active gold species

266 so as to stabilize the active species of Au_2Cl_6 , and then increase the long-term stability of
267 Au-based catalysts in acetylene hydrochlorination.⁴⁴ Additionally, the DFT calculations
268 indicated that the species RuCl_3 could not activate efficiently the reactants of acetylene
269 and hydrogen chloride.⁴⁵ In combination with the activity of Ru catalysts (Fig. 2), the
270 variation of Ru species on N-doped supports (Table 5) and the contents of N species in
271 the supports (Table 3), it is reasonable to conclude that the pyridine-nitrogen (N_p) plays
272 an important role in augment of the catalytic activity of Ru-supported catalysts.

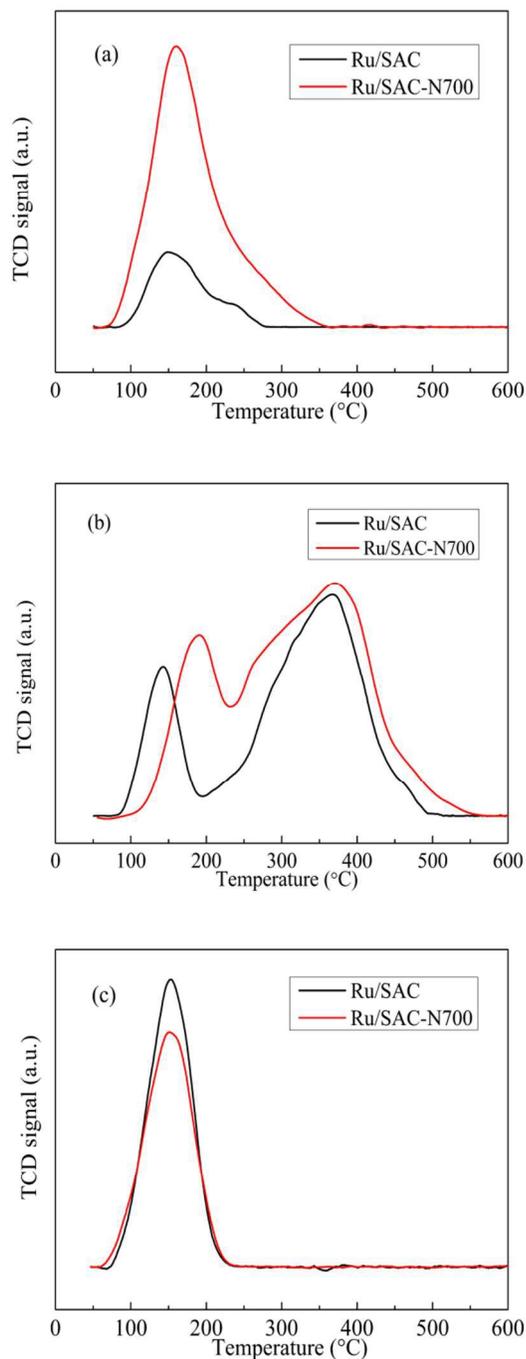


273
274 **Fig. 5** H_2 TPR profiles of fresh catalysts: (a) Ru/SAC, (b) Ru/SAC-N600, (c) Ru/SAC-N700, (d)
275 Ru/SAC-N800

276 Fig. 5 displays the TPR profiles of the fresh Ru-based catalysts. The broad peak in
277 the range of 400-700 °C is attributed to the reduction of functional groups on the support.
278 For the fresh Ru/SAC catalyst, it exhibits the peak at 183 °C together with a shoulder at
279 291 °C, which is attributed to the reduction of RuCl_3 and RuO_2 , respectively.^{13, 14, 17, 46}
280 For the Ru/SAC-N catalysts, the two peaks shift to higher temperature and the peak
281 intensity around 295 °C becomes stronger, with the maximum peak intensity
282 corresponding to Ru/SAC-N700. The results suggesting that the N-dopants strengthen the

283 interaction between the supports and RuO₂ and RuCl₃ species.

284 TPD is an effective technique to study the effects of N-dopants on the adsorption
285 properties of reactants and the product on the Ru-based catalysts. Fig. 6 displays the C₂H₂,
286 HCl and C₂H₃Cl TPD profiles of the Ru/SAC and Ru/SAC-N700. The peak area
287 indicates the adsorption capacity and the desorption temperature reflects the adsorption
288 strength. As shown in Fig. 6a, the HCl desorption temperature is 150 °C on Ru/SAC,
289 159 °C on Ru/SAC-N700, and the adsorption capacity of HCl on Ru/SAC-N700 is much
290 larger than that on Ru/SAC. For another reactant C₂H₂, the catalyst Ru/SAC-N700 also
291 shows larger adsorption capacity, comparing with Ru/SAC (Fig. 6b). The trend of TPD
292 profile for the product C₂H₃Cl is opposite with that of C₂H₂ and HCl, i.e., the adsorption
293 capacity for C₂H₃Cl on Ru/SAC-N700 is smaller than that on Ru/SAC (Fig. 6c).
294 Therefore, N-dopants can enhance the adsorption of reactants and the desorption of the
295 product, consequently results in higher catalytic activity of Ru/SAC-N700.



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Fig. 6 TPD profiles of the catalysts: (a) HCl-TPD, (b) C₂H₂-TPD, (c) C₂H₃Cl-TPD

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Further, TG was used to evaluate the degree of coke deposition on the surface of Ru-based catalysts. As shown in Fig. S6, both fresh and used catalysts have a slight weight loss before 100 °C, owing to water desorption. In the range of 100-400 °C, the

301 used catalysts exhibit an obvious weight loss (5.0%). When the temperature exceeds
302 400 °C, the fresh and used catalysts rapidly decrease in weight because the combustion of
303 activated carbon. Taking into account the carbon support can lose its weight by reacting
304 with oxygen in air to produce CO₂, the coke deposition is calculated by the difference of
305 weight loss of the fresh and used catalyst in the temperature range of 100-400 °C.⁴⁷⁻⁴⁹
306 Based on this method, the coke deposition of the catalysts is calculated and listed in
307 Table 6.

308 As listed in Table 6, the Ru/SAC-N700 catalyst has the least coke deposition of
309 2.6%. The amount of coke deposition increases in the order: Ru/SAC-N700 (2.6%) <
310 Ru/SAC-N800 (3.3%) < Ru/SAC-N600 (3.6%) < Ru/SAC (4.3%). This result is
311 consistent with the order of catalytic activity of Ru-supported catalysts. Combining with
312 the TPD profiles (Fig. 6), it is suggested that the larger adsorption capacities of HCl and
313 C₂H₂, as well as the easier desorption of C₂H₃Cl result in the significant reduction of coke
314 deposition on Ru catalysts with the N-doped support.

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Table 6 Coke deposition of the catalysts

Samples	Amount of coke deposition (%)
Ru/SAC	4.3
Ru/SAC-N600	3.6
Ru/SAC-N700	2.6
Ru/SAC-N800	3.3

317

318 4. Conclusion

319 Ru-based catalysts with the support of N-doped spherical active carbon were
320 prepared and assessed for acetylene hydrochlorination. The optimal catalyst
321 Ru/SAC-N700 shows the acetylene conversion of 99.8% at the conditions of 170 °C,

322 C₂H₂ GHSV 180 h⁻¹ and V(HCl):V(C₂H₂)=1.1:1. It is indicated that the pyridine-nitrogen
323 plays an important role in augment of the catalytic activity of Ru-based catalysts.
324 N-dopants can greatly increase the amount of the component RuO₂ in Ru catalysts,
325 enhance the adsorption of reactants and the desorption of the product, and reduce
326 significantly the coke deposition, consequently resulting in higher catalytic activity of
327 Ru/SAC-N700. These results provide a potential route to explore high efficient Ru-based
328 catalysts for acetylene hydrochlorination.

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