

1           **Oxidation modification of Ru-based catalyst for**  
2           **acetylene hydrochlorination**

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19 **Figure S7.** TEM images of the fresh and used catalysts: (a) Fresh Ru/AC, (b) Used  
20 Ru/AC, (c) Fresh Ru/AC-O, (d) Used Ru/AC-O, (e) Fresh (Ru/AC)-O, (f) Used  
21 (Ru/AC)-O, (g) Fresh Ru-O/AC-O, (h) Used Ru-O/AC-O.

22 **Table S1** The catalytic performance of some potential non-mercury catalysts recently reported in the literatures.

Catalyst	Composition of catalysts	Reaction conditions	Initial catalytic activity <sup>a</sup>	Deactivation rate (% h <sup>-1</sup> ) <sup>b</sup>
Mo <sub>2</sub> N/AC <sup>[1]</sup>	1.5 wt% MoN	T = 180 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 30 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.15	X <sub>A</sub> = 80.0%, S <sub>VCM</sub> > 90.0%	4.28
Au-Bi/C <sup>[2]</sup>	0.30 wt% Au, n(Bi)/n(Au) = 3	T = 180 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 600 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.1	X <sub>A</sub> = 87.0%, S <sub>VCM</sub> > 99.0%	0.500
PdCl <sub>2</sub> -KCl-LaCl <sub>3</sub> /C <sup>[3]</sup>	0.9 wt% Pd, 0.2 wt% KCl, 0.2 wt% LaCl <sub>3</sub>	T = 120-180 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 120 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.15	X <sub>A</sub> = 98.0%, S <sub>VCM</sub> > 99.5%	10.500
Z4M1 <sup>[4]</sup>	1.5 at% N	T = 180 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 50 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.15	X <sub>A</sub> = 60.0%, S <sub>VCM</sub> > 90.0%	0.300
Ru-in-CNT <sup>[5]</sup>	1 wt% Ru	T = 170 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 90 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.1	X <sub>A</sub> = 99.8%, S <sub>VCM</sub> > 99.0%	0.480
Ru-O/AC-O	1 wt% Ru	T = 180 °C. GHSV(C <sub>2</sub> H <sub>2</sub> ) = 180 h <sup>-1</sup> , V <sub>HCl</sub> /V <sub>C2H2</sub> = 1.15	X <sub>A</sub> = 99.6%, S <sub>VCM</sub> > 99.9%	0.275

23 <sup>a</sup> X<sub>A</sub> represents the initial conversion of acetylene and S<sub>VCM</sub> represents the selectivity to VCM of the catalyst.

24 <sup>b</sup> Deactivation rate was defined as (the initial maximum C<sub>2</sub>H<sub>2</sub> conversion – the final C<sub>2</sub>H<sub>2</sub> conversion)/(deactivation period, h)

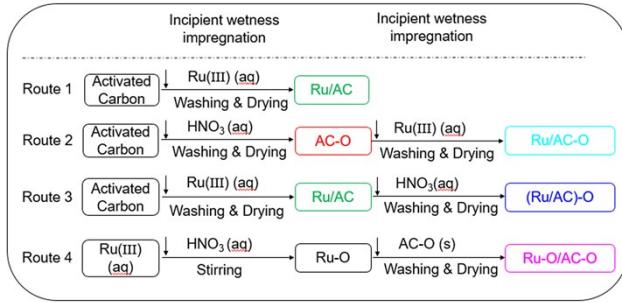
25 **Table S2** The relative content of the elements in the catalysts, determined by XPS spectra.

Catalysts	Ru (wt%)	O (wt%)	C (wt%)	Others (wt%)
Fresh AC	---	13.42	85.75	0.83
Used AC	---	5.68	93.53	0.79
Fresh AC-O	---	22.33	77.05	0.62
Used AC-O	---	15.05	84.37	0.58
Fresh Ru/AC	0.98	11.57	86.98	0.47
Used Ru/AC	0.92	6.46	92.23	0.39
Fresh Ru/AC-O	0.96	18.43	80.02	0.59
Used Ru/AC-O	0.91	13.51	85.06	0.52
Fresh (Ru/AC)-O	0.95	19.32	79.01	0.72
Used (Ru/AC)-O	0.93	14.85	83.56	0.66
Fresh Ru-O/AC-O	0.97	20.29	78.28	0.46
Used Ru-O/AC-O	0.95	17.58	81.09	0.38

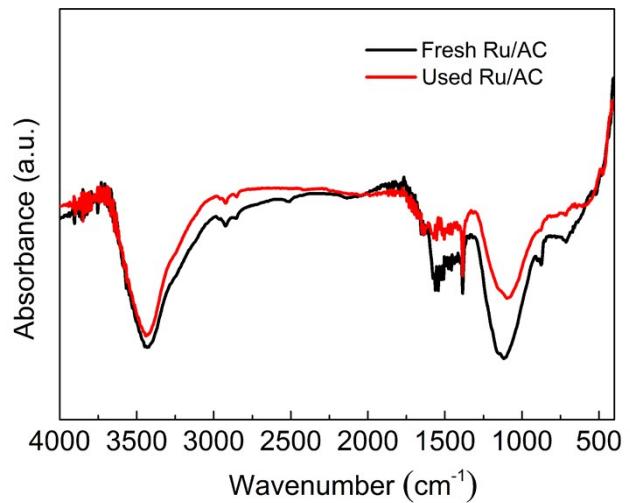
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29 **Figure S1.** The schematic diagram of four different routes to synthesize Ru-based catalysts.



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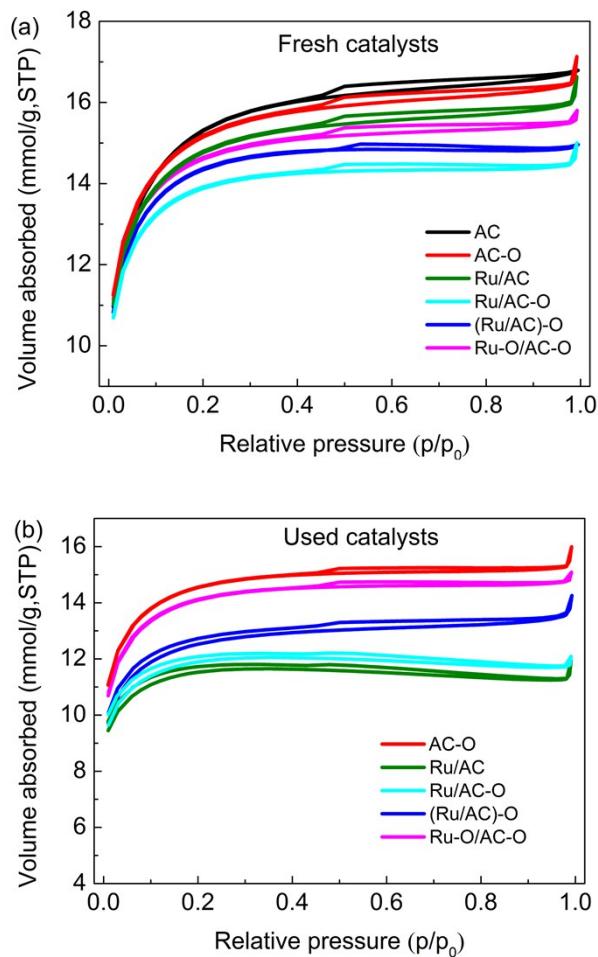


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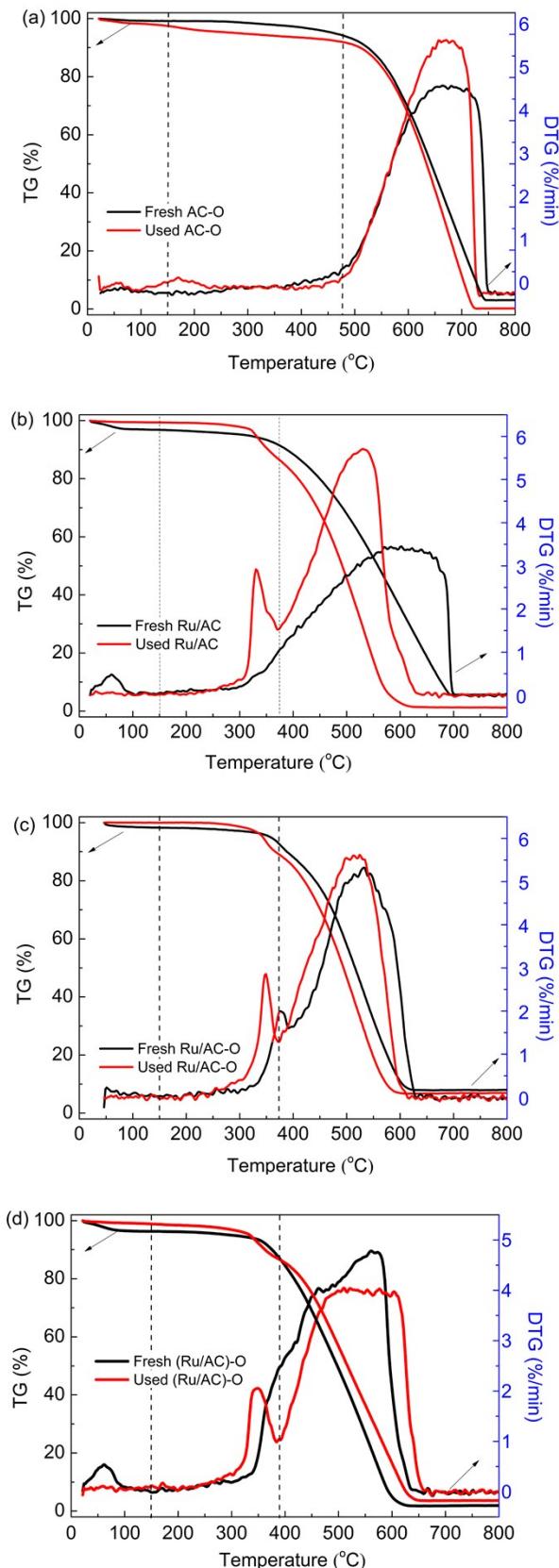
**Figure S2.** FT-IR spectra of the fresh and used Ru/AC catalysts.

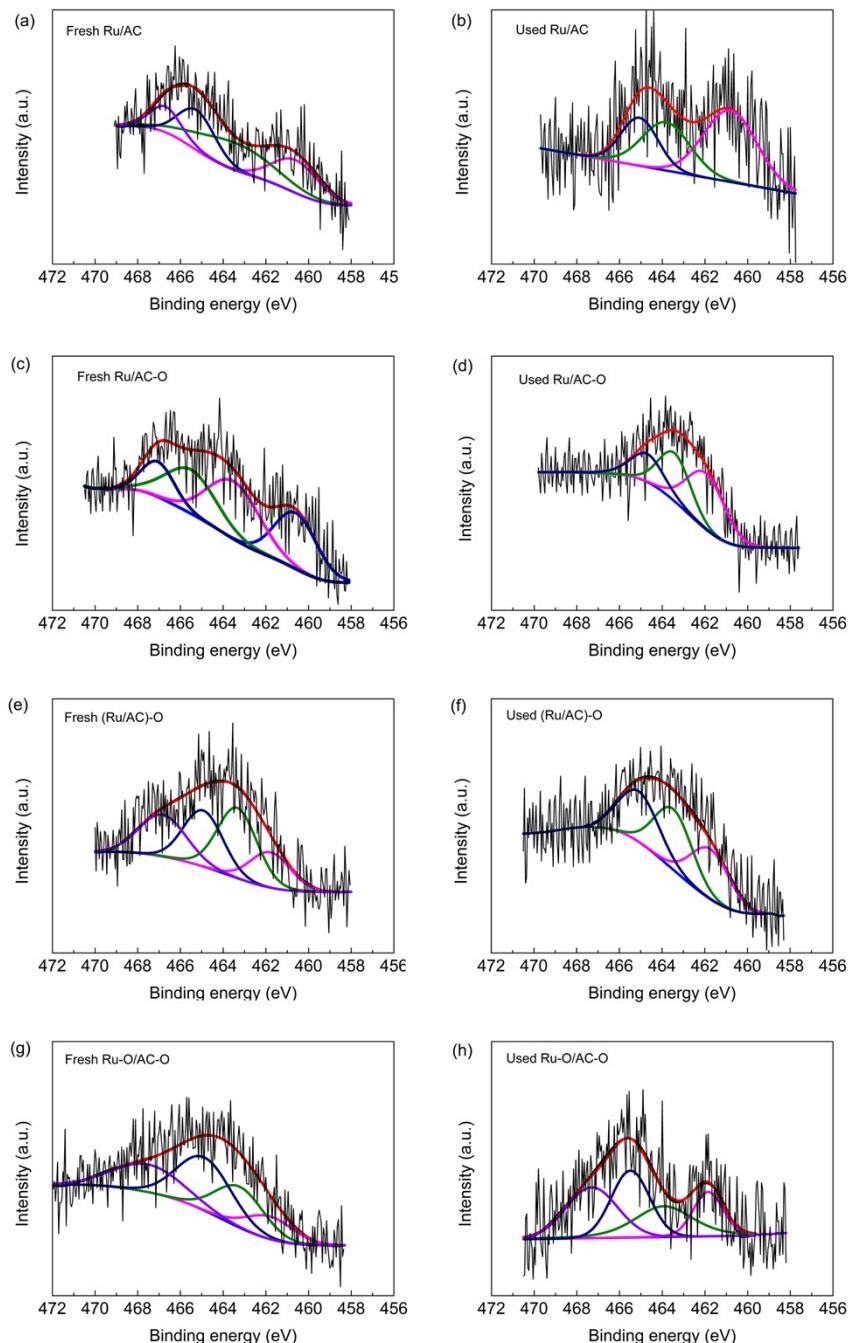
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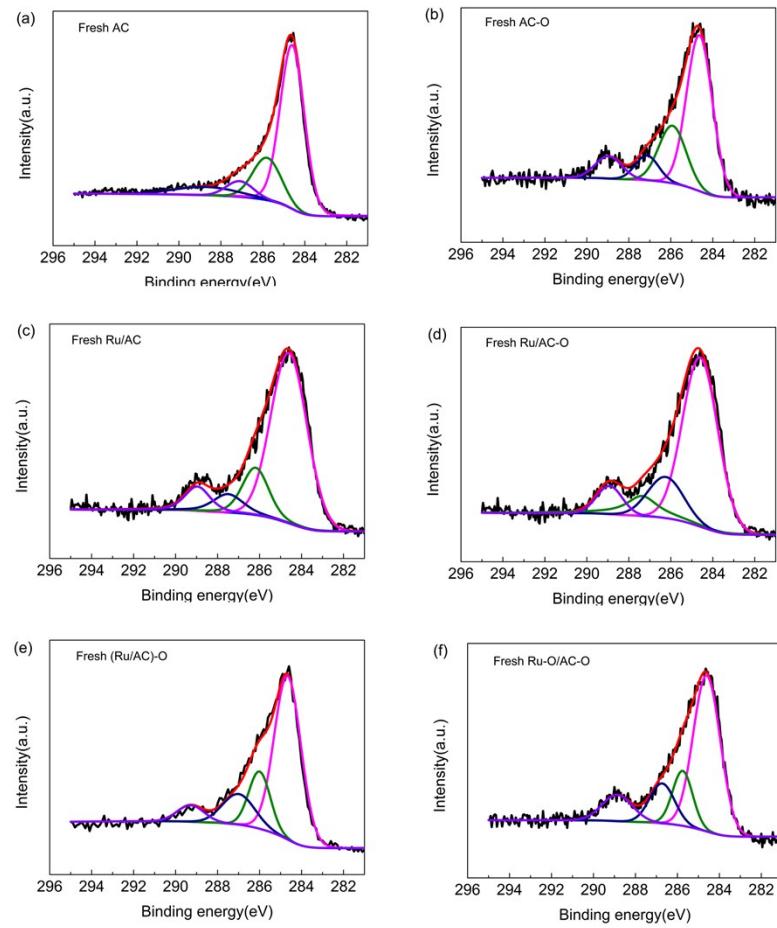
37 **Figure S3.** Nitrogen adsorption-desorption isotherms of the fresh (a) catalysts and used (b)  
38 catalysts.

**Figure S4.** TG curves of fresh and used catalysts recorded in air atmosphere.



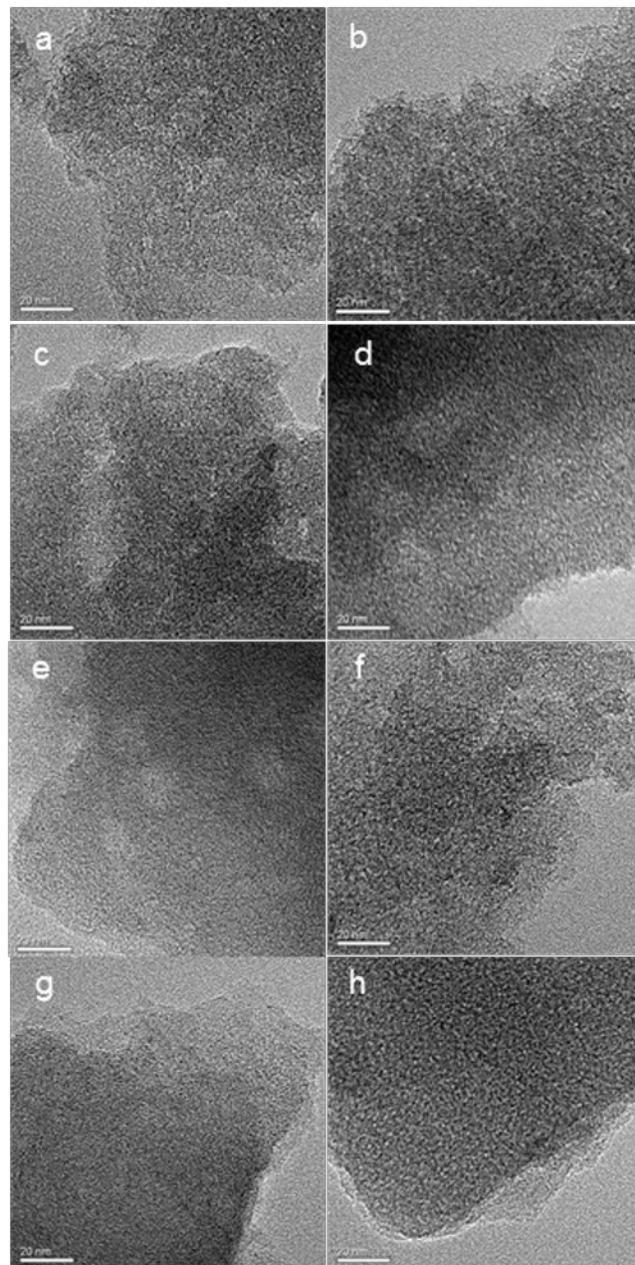
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44 **Figure S5.** High-resolution XPS spectra of Ru 3p for the fresh and used Ru-based catalysts.



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**Figure S6.** XPS spectra of C 1s for the fresh catalysts.



51 **Figure S7.** TEM images of the fresh and used catalysts: (a) Fresh Ru/AC, (b) Used Ru/AC, (c)  
52 Fresh Ru/AC-O, (d) Used Ru/AC-O, (e) Fresh (Ru/AC)-O, (f) Used (Ru/AC)-O, (g) Fresh Ru-  
53 O/AC-O, (h) Used Ru-O/AC-O.

55 **References**

- 56 [1] H. Dai, M. Zhu, H. Zhang, F. Yu, C. Wang and B. Dai, *J. Ind. & Eng. Chem.*,  
57 2017.
- 58 [2] K. Zhou, J. Jia, C. Li, H. Xu, J. Zhou, G. Luo, F. Wei, *Green Chem.*, 2015, **17**,  
59 356-364.
- 60 [3] Q. Song, S. Wang, B. Shen, J. Zhao, *Pet. Sci. Technol.*, 2010, **28**, 1825-1833.
- 61 [4] X. Li, J. Zhang and W. Li, *J. Ind. & Eng. Chem.*, 2016, **44**, 146-154.
- 62 [5] G. Li, W. Li, H. Zhang, Y. Pu, M. Sun and J. Zhang, *Rsc Adv.*, 2014, **5**, 9002-9008.