Supplementary Information for

Non-mercury catalytic acetylene hydrochlorination over bimetallic Au-Ba(II)/AC catalysts

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Catalyst characterization

Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing the catalyst powder in high-purity ethanol, and then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300-mesh copper TEM grid. Bright-field and annular dark-field (ADF) imaging experiments were respectively carried out using a JEM2100F TEM instrument and an FEI Titan 80-300 TEM/STEM system equipped with a CEOS spherical aberration corrector.

X-ray photoelectron spectroscopy (XPS) was performed with a PHI5000 Versa Probe spectrometer using a monochromatised Al Kα X-ray source (24.2 W) with an analyzer pass energy of 187.85 eV for survey scans and 46.95 eV for detailed elemental scans. Binding energies were referenced to the C1s binding energy of carbon, taken to be 284.6 eV. As it is well known that cationic Au species can be reduced to the zero-valent state by secondary electron emission during XPS analysis, the Au(4f) region was recorded at the beginning and end of the analysis.[1] The Au^{3+}, Au^{0}-s, and Au^{0} amounts are reported as the percentage of the total Au amount.

Au contents in the catalysts were determined using an inductively coupled plasma (ICP 725), using a Vista Chip IICCD detector, and the testing wavenumber is 242.794 nm.

Table S1 The loss ratio of Au in Au-Ba(II)/AC catalysts, determined by ICP-AES.

Catalyst	Au loading, wt %		Loss ratio of Au, %
	Fresh	Used	
Au/AC	0.908	0.899	0.99
Au1Ba(II)0.5/AC	0.915	0.906	0.98
Au1Ba(II)1/AC	0.918	0.910	0.87
Au1Ba(II)3/AC	0.912	0.902	1.10
Au1Ba(II)5/AC	0.907	0.898	0.99

Table S2 Weight loss of fresh and used Au/AC catalysts under different temperature ranges.

Temperature (°C)	< 150	150-450	450-500	150-500
Weight loss of fresh sample, (%)	0.9	1.6	2.6	4.2
Weight loss of used sample, (%)	0.8	5.5	3.4	8.9

Table S3 Weight loss of fresh and used Au1Ba(II)1/AC catalysts under different temperature ranges.

Temperature (°C)	< 150	150-400	400-450	150-450
Weight loss of fresh sample, (%)	1.0	3.6	2.7	6.3
Weight loss of used sample, (%)	0.6	6.4	2.8	9.2

66 **Table S4** Size of Au particles in Au-Ba(II)/AC catalysts, determined by XRD [a].

Catalyst	Au particles Size (nm)	
	Fresh	Used
Au/AC	23	36±3
Au1Ba(II)0.5/AC	32	33±3
Au1Ba(II)1/AC	<4 [b]	21±3
Au1Ba(II)3/AC	<4 [b]	32±3
Au1Ba(II)5/AC	<4 [b]	23±3

[a] Error estimated from XRD peak broadening of 0.06° at the Au (111) reflection at 38.10° (2θ).

[b] It was impossible to assign any error band below 4 nm, as this size is below the XRD method.

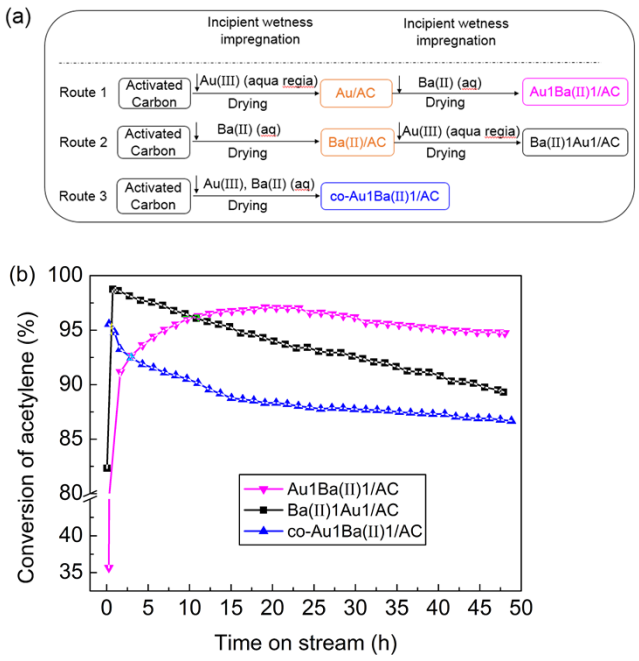


Fig. S1. (a) The schematic diagram of three different bimetallic catalysts prepared with different impregnation order of two precursors. (b) Catalytic performance of three kinds of bimetallic catalysts. Reaction conditions: T = 200 °C, GHSV(C_2H_2) = 360 h^{-1}, $V_{HCl}/V_{C_2H_2}$ = 1.15.

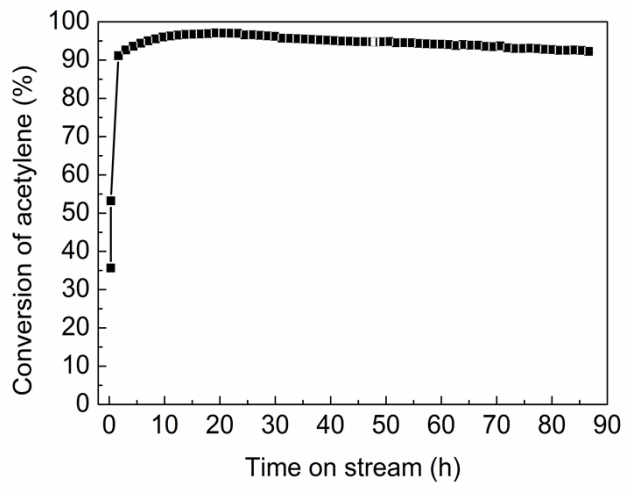
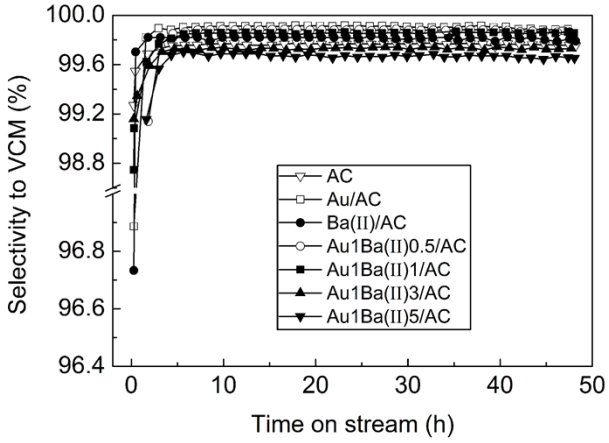


Fig. S2. Catalytic performance of Au1Ba(II)1/AC in 86 h on stream. Reaction conditions: T = 200 °C, GHSV(C_2H_2) = 360 h^{-1}, $V_{HCl}/V_{C_2H_2}$ = 1.15.



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77 **Fig. S3.** Selectivity to VCM over the fresh Au-Ba(II)/AC catalysts.

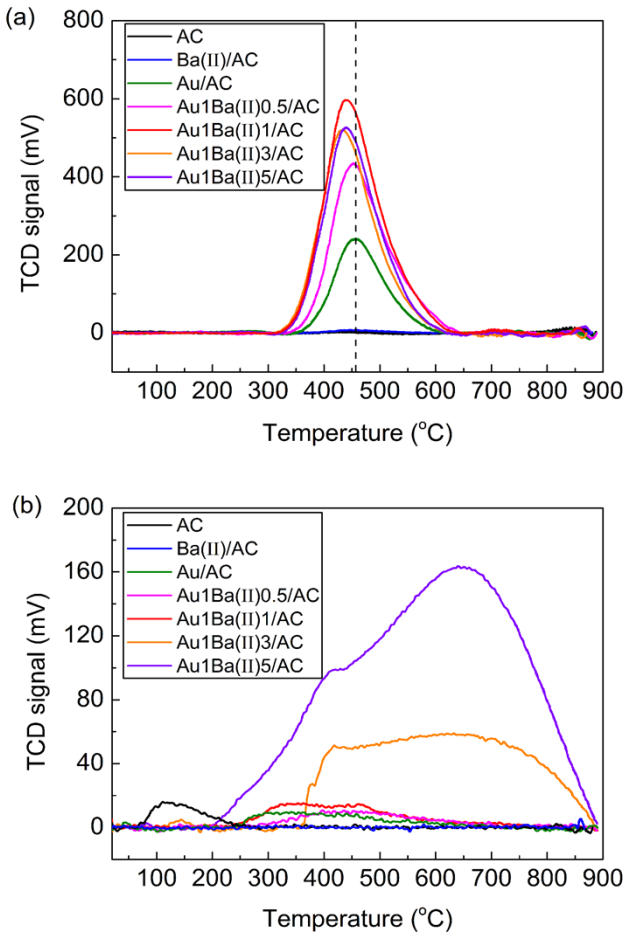


Fig. S4. (a) C_2H_2- and (b) HCl- TPD profiles of the fresh Au-Ba(II)/AC catalysts.

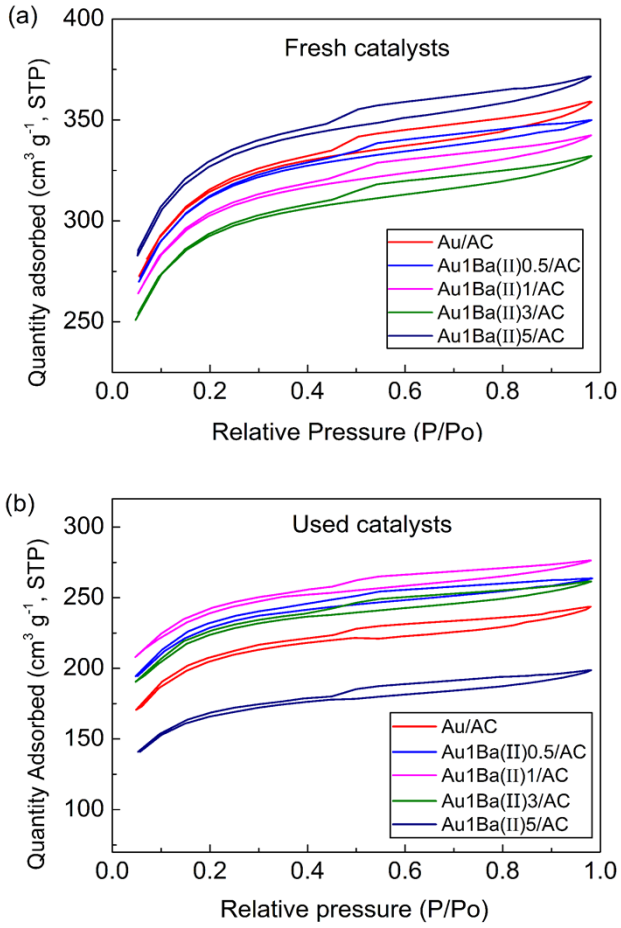
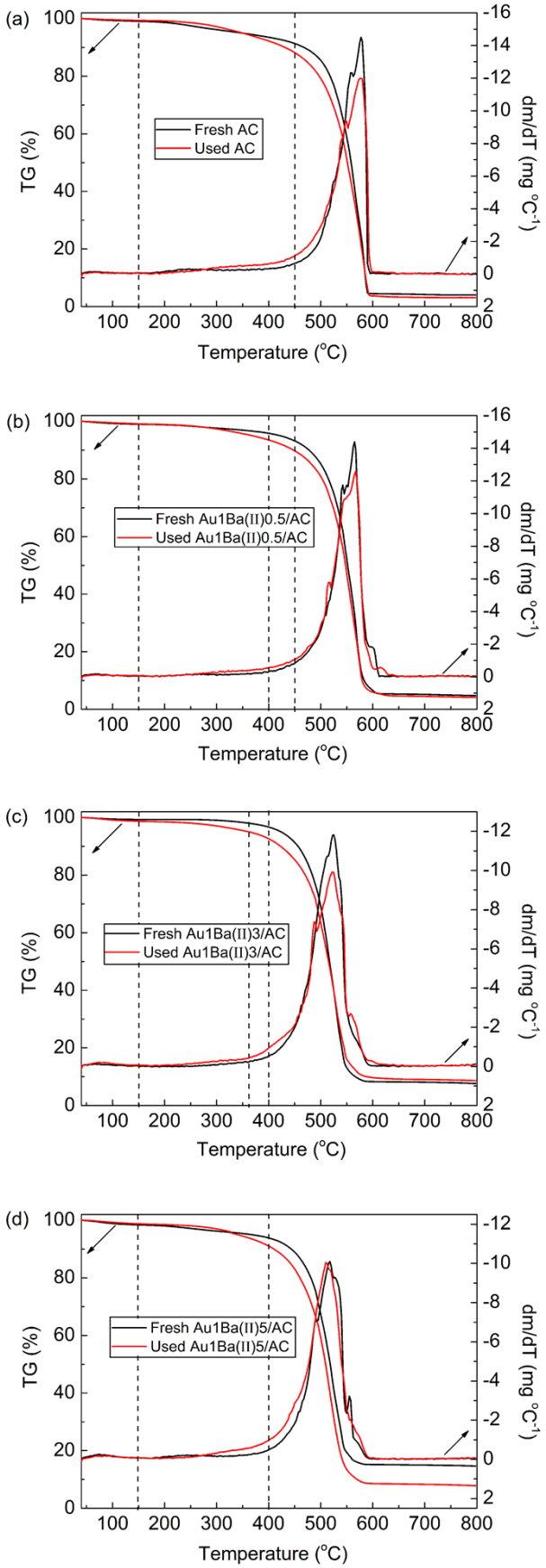


Fig. S5. Isothermal adsorption-desorption curves of (a) fresh and (b) used catalysts.

It can be seen from Fig. S5 that all of the samples exhibit type I isotherms with an H4 adsorption-desorption hysteresis loop based on IUPAC nomenclature, which is typically attributed to adsorption in the micropore.

The limiting adsorption quantity may sometimes indicate the monolayer adsorption capacity; it may also be the quantity that fills the pore volume for microporous adsorbents. The adsorption volume of each catalyst decreases after the hydrochlorination reaction (Fig. S5b), which is due to pore blockage brought about by carbon deposition or collapse. The adsorption of Au1Ba(II)1/AC changes minimally before and after the reaction, which indicates that the amount of carbon deposition or the degree of collapse in Au1Ba(II)1/AC is lower than that in other used catalysts.



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94 **Fig. S6.** TG curves of the fresh and used Au-Ba(II)/AC catalysts.

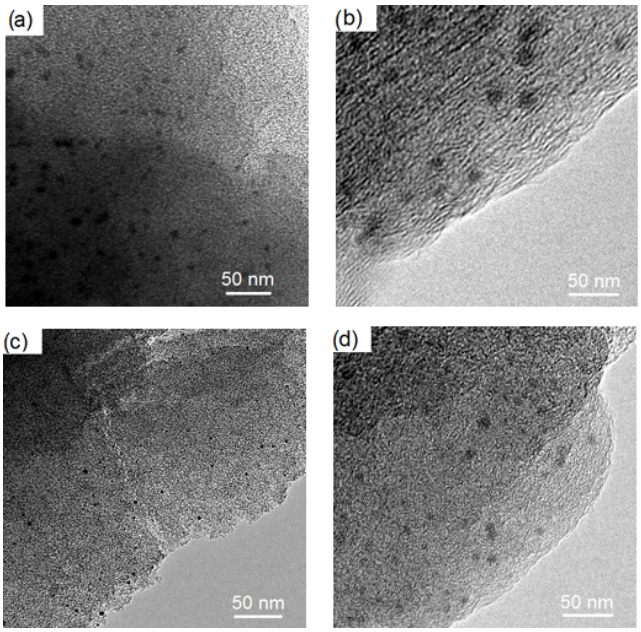

Fig. S7. TEM images of (a, b) Au/AC and (c, d) Au1Ba(II)1/AC before (a, c) and after (b, d) reaction.

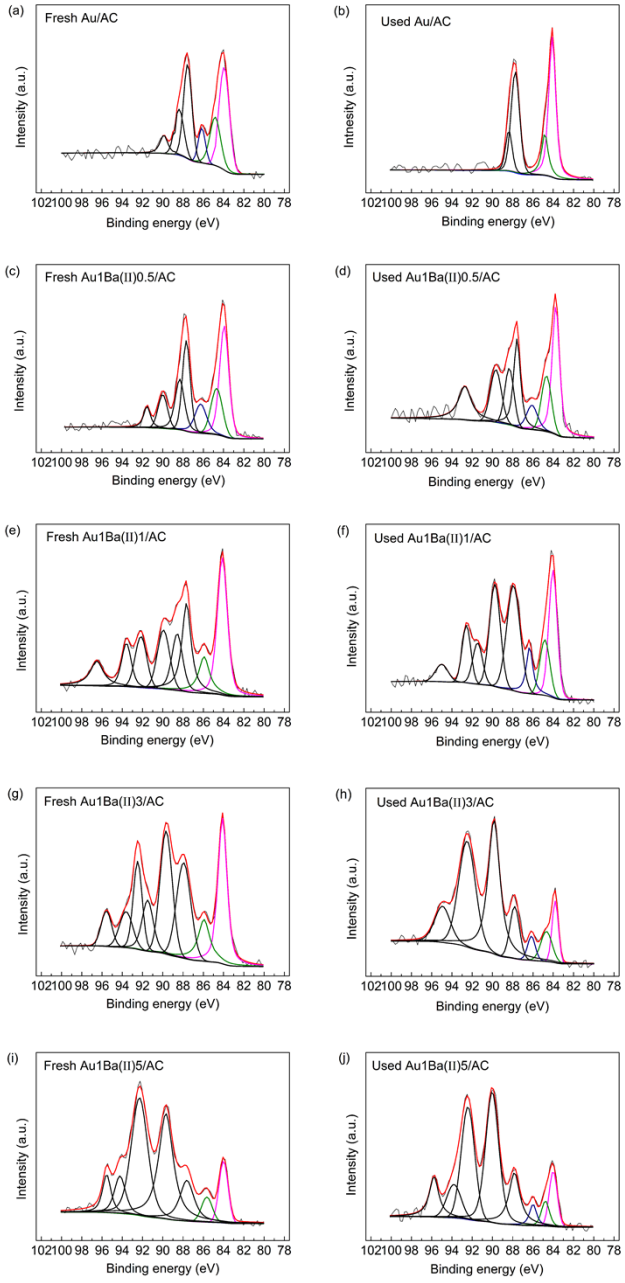

Fig. S8. Deconvolution profiles of XPS Au 4f7/2 spectra for Au-Ba(II)/AC catalysts. The spectra are relatively noisy because of low total loading of metals in the catalysts.

References

1. Y. Fong, B. R. Visser, J. R. Gascooke, B. C. C. Cowie, L. Thomsen, G. F. Metha, M. A. Buntine and H. H. Harris, *Langmuir*, 2011, **27**, 8099-8104.