Electronic Supplementary Information

Supported ionic-liquid-phase-stabilized Au(III) catalyst for acetylene hydrochlorination

Jia Zhao, Shanchuan Gu, Xiaolong Xu, Tongtong Zhang, Yi Yu, Xiaoxia Di, Jun NI, Zhiyan Pan, Xiaonian Li*

Industrial Catalysis Institute of Zhejiang University of Technology, State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Hangzhou, 310014, P.R. China

* Corresponding author. Tel: +86 571 88320002. E-mail address: xnli@zjut.edu.cn

Supplementary Figures

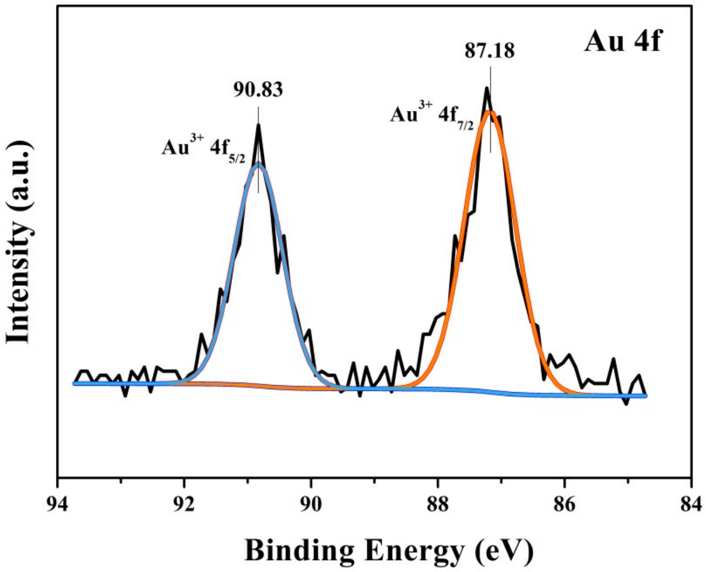


Fig. S1. XPS spectra of Au 4f of $[Prmim]AuCl_4$ complex.

After preparation, the $[Prmim]AuCl_4$ complex was analysed by XPS, Raman, UV-vis and FTIR. Fig. S1 shows the XPS spectra of the Au 4f photoelectron emission corresponding to the $[Prmin]AuCl_4$. The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ levels were located at 87.18 eV and 90.83 eV, respectively. The peaks attributed to the oxidation states of Au(III) species [1-2]. These showed that the metallic states of Au^0 was not present in the sample.

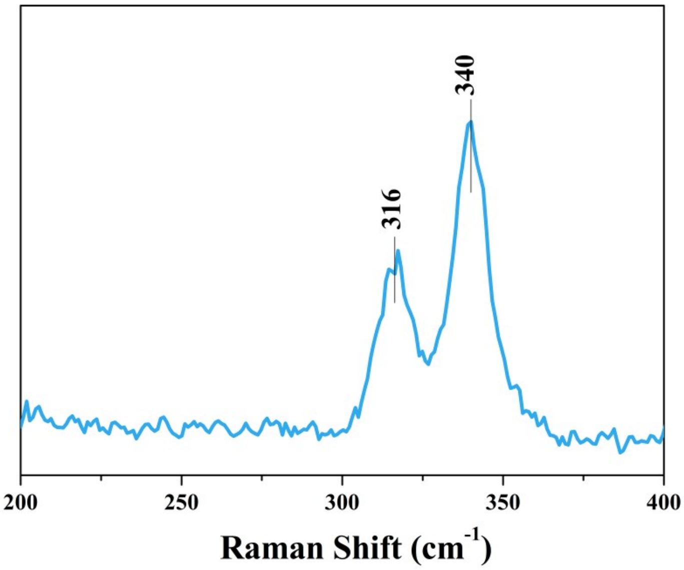


Fig. S2. Raman spectra of $[Prmim]AuCl_4$ complex.

Fig. S2 shows the Raman spectra of samples [Prmin]$AuCl_4$. The spectra of sample shows two peaks at 316 and 340 cm^{-1}, which are attributed to $AuCl_4^{—}$.[3]

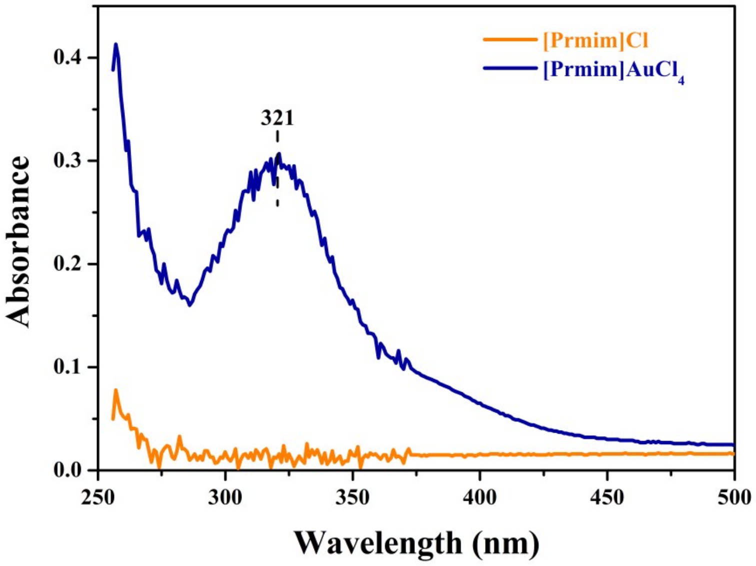


Fig. S3. UV-Vis spectra of [Prmim]$AuCl_4$ complex and pure [Prmim]Cl.

In Au(III) complexes, Au(III) is a d8 metal center where d-d electronic transitions result in UV-Vis absorption. The type and number of ligands interacting with the Au(III) center can be observed as intense bands in the UV region [4]. We employed UV–Vis spectrometer to analyze the [Prmim]$AuCl_4$ complex. As shown in Fig. S3, the absorption maximums of [Prmim]$AuCl_4$ complexe in chloroform appear at 321 nm. Furthermore, pure [Prmim]Cl hardly has UV absorption in the region (250-500 nm), so the absorption band is belong to $[AuCl_4]^-$.[5]

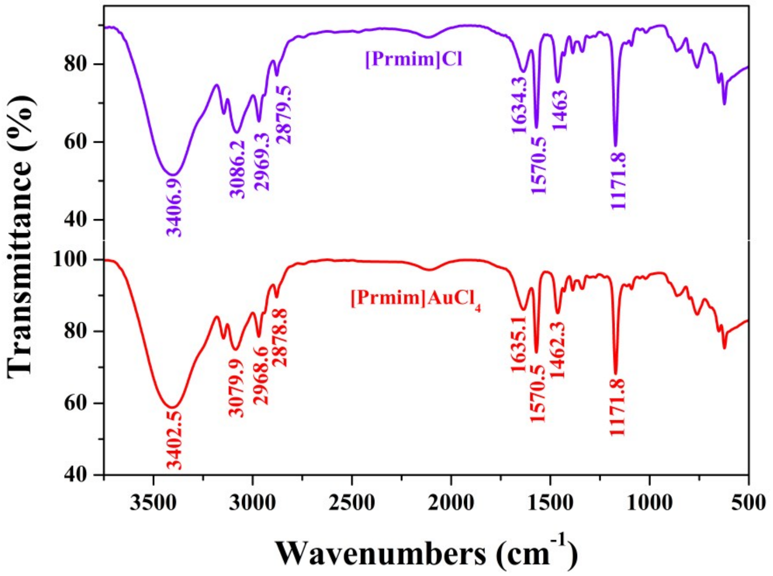


Fig. S4. Infrared spectra of [Prmim]AuCl$_4$ complex and pure [Prmim]Cl.

To obtain direct evidence of the interaction between [Prmim]Cl and AuCl$_4^-$, the FTIR measurement was employed to analyze the [Prmim]AuCl$_4$ complex, are shown in Fig. S4. The aliphatic C-H stretch peaks do not shift because of the weaker interaction between tetrachloroaurate anions and the alkyl side chains. However, the ring C-H stretch peaks shift to higher wavenumber about 6.3 cm^{-1}. The shift indicated bonding interaction between protons in the imidazolium cation and the Au metal center in the AuCl$_4^-$ anion.[5]

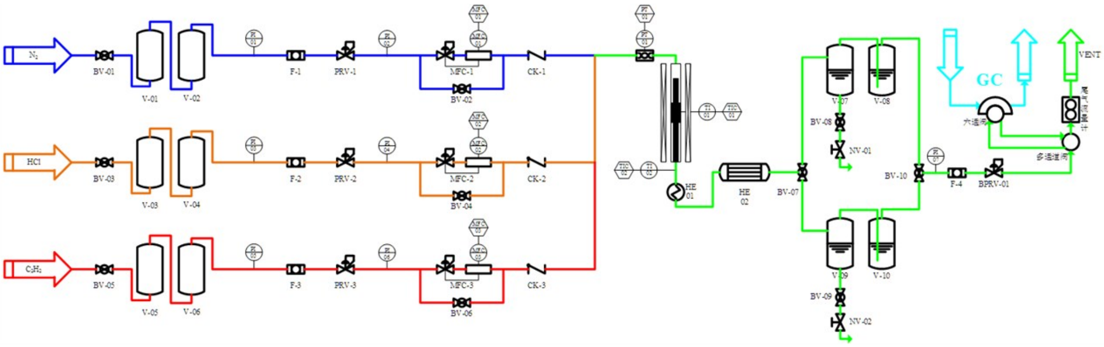
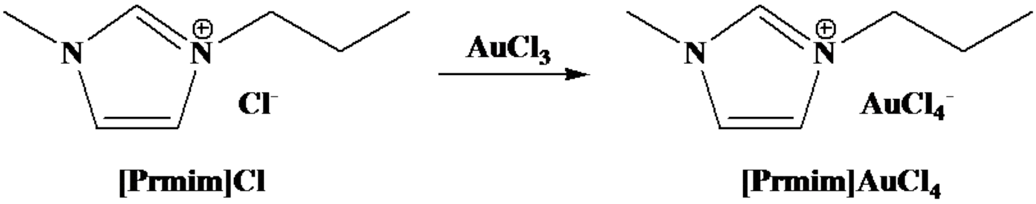


Fig. S5. Schematic representation of the experimental rig as applied in the here reported continuous flow, gas phase acetylene hydrochlorination experiments.



Scheme S6. The synthesis process of [Prmim]$AuCl_4$ complex.

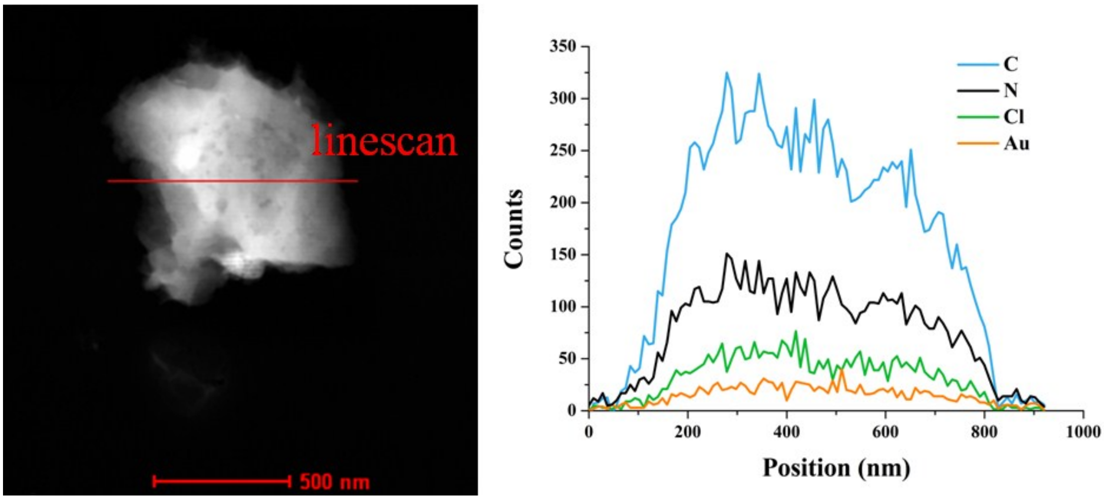


Fig. S7. TEM image of a Au-IL/AC catalyst (left) along with an EDX linescan, corresponding with the red line shown (right).

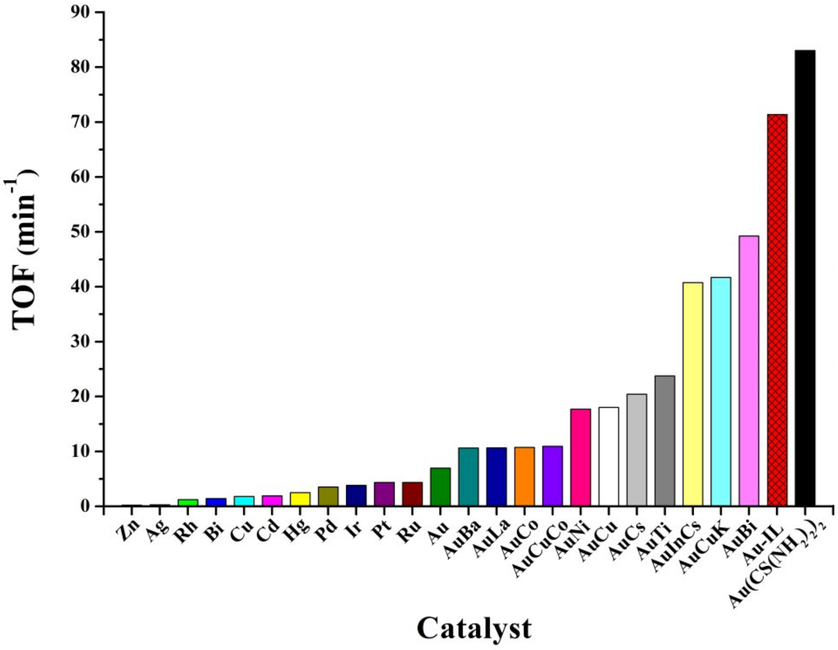
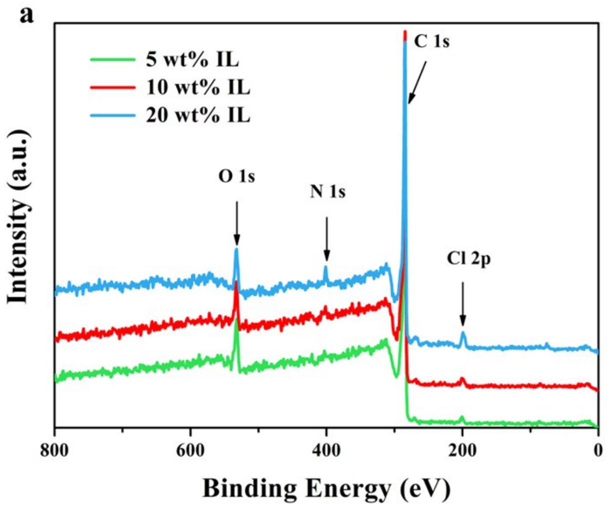


Fig. S8. The TOF value for the different catalysts: Au/AC,[6] Pt/AC,[7] Pd/AC,[6] Ru/AC,[8] Rh/AC,[6] Ir/AC,[7] Bi/AC,[9] Ag/AC,[6] Cu/AC,[10] Cd/AC,[6] Zn/AC,[6] Hg/AC,[6] AuBa/AC,[11] AuLa/AC,[12] AuCo/AC,[13] AuCuCo/AC,[14] Au/Ni,[15] AuCs/AC,[16] AuTiO$_2$/AC,[17] AuInCs/AC,[18] AuCuK/AC,[19] AuBi/AC[20] Au(CS(NH$_2$)$_2$)$_2$/AC,[21] and Au-IL/AC.



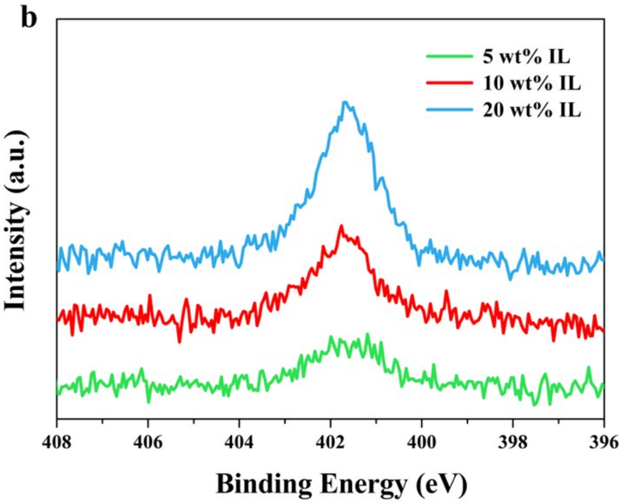


Figure S9. XPS spectra of (a) Au-IL/AC catalysts with different IL loading normalized at 284.8 eV of C1s, (b) N 1s spectrum.

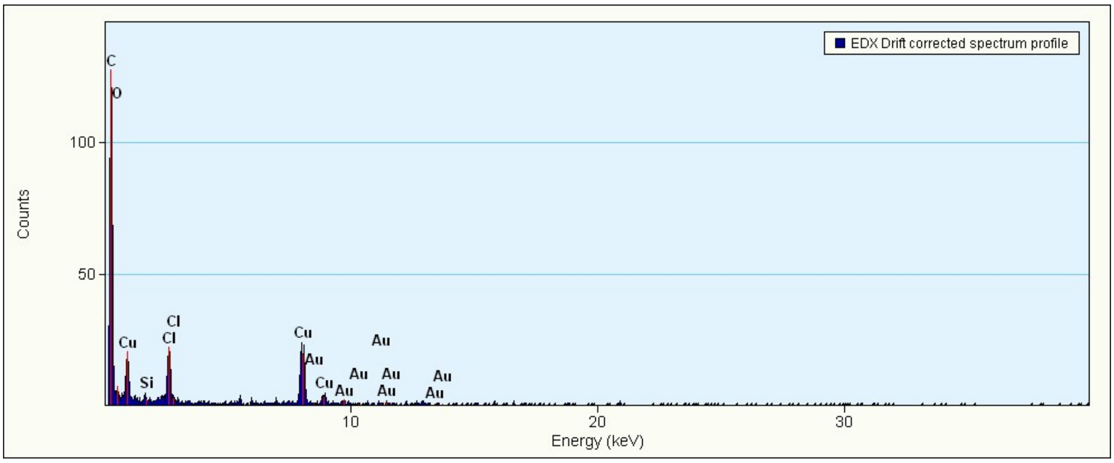


Figure S10. XEDS spectra of used Au-IL/AC catalyst

References

[1] M. Conte, C. J. Davies, D. J. Morgan, T. E. Davies, A. F. Carley, P. Johnston, *Catal. Sci. Technol.* **2013**, *3*, 128-134.

[2] M. Conte, C. J. Davies, D. J. Morgan, A. F. Carley, P. Johnston, G. J. Hutchings, *Catal. Lett.* **2014**, *144*, 1-8.

[3] L. F. Bobadilla, T. Blasco and J. A. Odriozola, *Phys. Chem. Chem. Phys.* **2013**, *15*, 16927-16934.

[4] A. Usher, D. C. McPhail, J. Brugger, *Geochim. Cosmochim. Acta.* **2009**, *73*, 3359-3380.

[5] Y. Tong, H. X. Yang, J. Li, Y. Z. Yang, *Sep. Purif. Technol.* **2013**, *120*, 367-372.

[6] B. Nkosi, N. J. Coville, G. J. Hutchings, *J. Chem. Soc. Chem. Commun.* **1988**, *1*, 71-72.

[7] B. Nkosi, M. D. Adams, G. J.Hutchings, *J. Catal.* **1991**, *128*, 378-386.

[8] Y. Pu, J. Zhang, L. Yu, Y. Jin, W. Li, *Appl. Catal. A: Gen.* **2014**, *488*, 28-36.

[9] K. Zhou, J. Jia, X. Li, X. Pang, C. Li, J. Zhou, G. Luo, F. Wei, *Fuel Process Technol.* **2013**, *108*, 12-18.

[10] K. Zhou, J. Si, J. Jia, J. Huang, J. Zhou, G. Luo, F. Wei, *RSC Adv.* **2014**, *4*, 7766-7769.

[11] H. Zhang, W. Li, X. Li, W. Zhao, J. Gu, X. Qi, Y, Dong, B. Dai, J. Zhang, *Catal. Sci. Technol.* **2015**, *5*, 1870-1877.

[12] H. Zhang, B. Dai, X. Wang, L. Xu, M. Zhu, *J. Ind. Eng. Chem.* **2012**, *18*, 49-54.

[13] H. Zhang, B. Dai, X. Wang, W. Li, Y. Han, J. Gu, J. Zhang, *Green Chem.* **2013**, *15*, 829-836.

[14] H. Zhang, B. Dai, W. Li, X. Wang, J. Zhang, M. Zhu, J. Gu. *J. Catal.* **2014**, *316*, 141-148.

[15] Y. Pu, J. Zhang, X. Wang, H. Zhang, L. Yu, Y. Dong, W. Li, *Catal. Sci. Technol.* **2014**, *4*, 4426-4432.

[16] J. Zhao, J. Xu, J .Xu, T. Zhang, X. Di, X .Li, J, Ni, X. Li, *RSC Adv.* **2015**, *5*, 6925-6931.

[17] C. Huang, M. Zhu, L. Kang, X. Li, B. Dai, *Chem. Eng. J.* **2014**, *242*, 69-75.

[18] J. Zhao, T. Zhang, X. Di, J. Xu, S. Gu, Q. Zhang, J. Ni, X. Li, *Catal. Sci. Technol.* **2015**, *5*, 4973-4984.

[19] K. Zhou, J. Jia, C. Li, H. Xu, J. Zhou, G. Luo, F. Wei, *Green Chem.* **2015**,*17*, 356-364.

[20] K. Zhou, W. Wang, Z. Zhao, G. Luo, J. T. Miller, M. S. Wong, F. Wei, *ACS Catal.* **2014**, *4*, 3112-3116.

[21] P. Johnson, N. Carthey, G. J.Hutchings, *J. Am. Chem. Soc.* **2015**,*137*, 14548-14557.