



**Figure S1.** XPS spectra (a) and X-ray excited Auger electron spectroscopy (XAES) spectra (b) of the catalysts after reaction after reaction.

It can be seen from Figure S1a that, compared with the fresh catalysts, the BE value of  $\text{Cu}2p_{3/2}$  shifts to around 932.2 eV and the satellite peak disappears. This phenomenon is due to the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  and/or  $\text{Cu}^0$  [1]. Because of the similar BE value between  $\text{Cu}^+$  and  $\text{Cu}^0$  species, it is hard to distinguish the copper species with low valence via using XPS. Therefore, the Cu LMM XAES spectrum is employed to discriminate the copper species. As displayed in Figure S1b, the symmetric Auger kinetic energy peak at around 916.6 eV corresponding to  $\text{Cu}^+$  species could be observed [1,2], indicating only  $\text{Cu}^+$  species exists on the catalysts.

## References

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2. Li, H.T.; Ban, L.J.; Wang, Z.P.; Meng, P.F.; Zhang, Y.; Wu, R.F.; Zhao, Y.X. Regulation of Cu species in  $\text{CuO}/\text{SiO}_2$  and its structural evolution in ethynylation reaction. *Nanomaterials*. **2019**, *9*, 842–857.