*Supporting information*

# Novel nonmetal catalyst of supported tetraphenylphosphonium bromide for acetylene hydrochlorination

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**Table S1** The charge variations in atoms of HCl, $C_2H_2$ and $C_2H_3Cl$ adsorbed on TPPB.

| | Atoms | Before adsorption (e) | After Adsorption (e) | **Δ**(e) |
|---|---|---|---|---|
| HCl | Cl | -0.123 | -0.272 | -0.149 |
| | H1 | 0.123 | 0.048 | -0.074 |
| $C_2H_2$ | C1 | -0.093 | -0.085 | 0.008 |
| | C2 | -0.093 | -0.127 | -0.035 |
| | H2 | 0.093 | 0.058 | -0.035 |
| | H3 | 0.093 | 0.078 | -0.015 |
| $C_2H_3Cl$ | H1 | 0.050 | 0.033 | -0.016 |
| | Cl | -0.067 | -0.082 | -0.015 |
| | C1 | -0.081 | -0.071 | 0.010 |
| | C2 | -0.008 | -0.023 | -0.015 |
| | H2 | 0.052 | 0.052 | 0.000 |
| | H3 | 0.054 | 0.045 | -0.008 |

**Table S2** The dihedral angle variations between atoms of HCl and $C_2H_2$ adsorbed on TPPB.

| | Dihedral Angle between atoms (º) | | | |
|---|---|---|---|---|
| | C2-C3-P7-C8 | C9-C8-P7-C19 | C18-C19-P7-C24 | C23-C24-P7-C3 |
| Free TPPB | -69.546 | -48.563 | -176.300 | -153.375 |
| TPPB-$C_2H_2$ | -69.346 | -49.383 | -167.562 | -160.655 |
| Δ change | 0.201 | -0.819 | 8.737 | -7.279 |
| TPPB-HCl | -69.950 | -47.696 | -170.516 | -157.465 |
| Δ change | -0.404 | 0.868 | 5.783 | -4.090 |

The atomic numbers of HCl, $C_2H_2$ and TPPB can be seen in Figure S1.

**Table S3** The charge variations of atoms and molecules for the reactants and the product during the reaction.

| Molecule | Atom | Free | Co-ads | Δe (atom) (Co-ads - Free) | Δe (molecule) (Co-ads - Free) | IM | Δe (atom) (IM - Co-ads) | Δe (molecule) (IM - Co-ads) | TS | Δe (atom) (TS - IM) | Δe (molecule) (TS - IM ) | Pr-ads | Δe (atom) (Pr-ads - TS) | Δe (molecule) (Pr-ads - TS) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_2$ | H2 | 0.093 | 0.062 | -0.031 | -0.060 | 0.084 | 0.023 | 0.020 | 0.094 | 0.010 | 0.197 | 0.052 | -0.042 | 0.273 |
| | C1 | -0.093 | -0.086 | 0.007 | | -0.109 | -0.023 | | -0.071 | 0.038 | | -0.071 | 0.000 | |
| | C2 | -0.093 | -0.118 | -0.025 | | -0.070 | 0.048 | | 0.059 | 0.129 | | -0.023 | -0.082 | |
| | H3 | 0.093 | 0.082 | -0.011 | | 0.054 | -0.027 | | 0.075 | 0.020 | | 0.045 | -0.029 | |
| HCl | Cl | -0.123 | -0.255 | -0.132 | -0.204 | -0.603 | -0.348 | -0.325 | -0.521 | 0.082 | 0.055 | -0.082 | 0.439 | |
| | H1 | 0.123 | 0.051 | -0.072 | | 0.074 | 0.022 | | 0.047 | -0.027 | | 0.033 | -0.013 | |
| TPPB | $Br^-$ | -0.668 | -0.478 | 0.190 | 0.264 | -0.146 | 0.331 | 0.305 | -0.398 | -0.251 | -0.252 | -0.634 | -0.236 | -0.273 |
| | $PPh^{4+}$ | 0.668 | 0.742 | 0.074 | | 0.716 | -0.026 | | 0.715 | -0.001 | | 0.678 | -0.037 | |

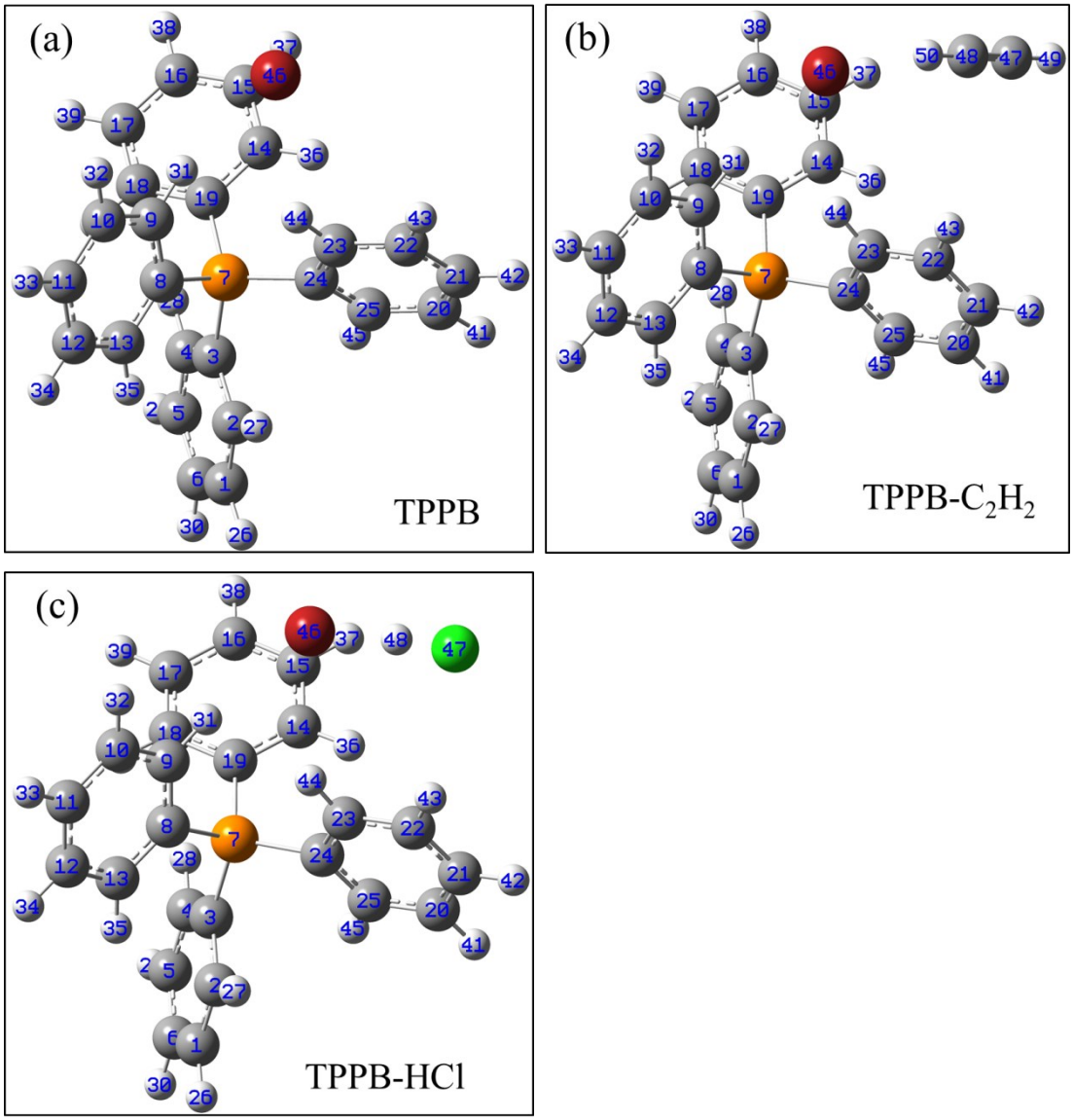


**Fig. S1** The stable structures of TPPB (a), TPPB-$C_2H_2$ (b) and TPPB-HCl (c). Carbon, hydrogen, bromine, phosphorus and chlorine atoms are depicted in gray, white, red, orange and green, respectively.

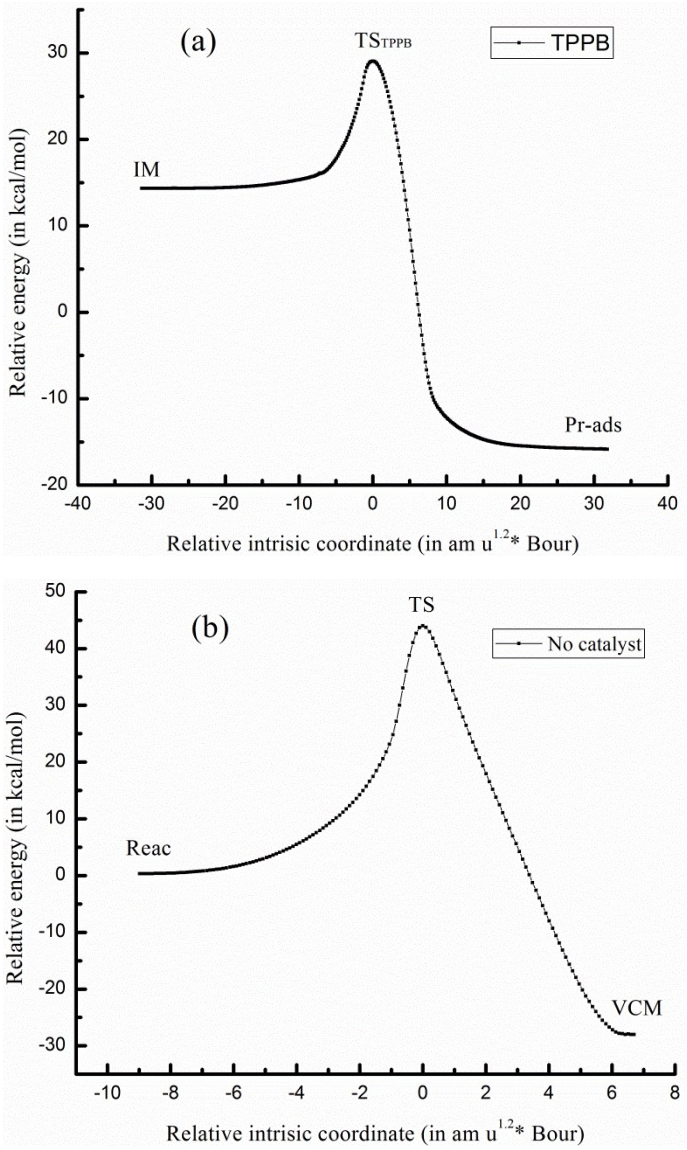


**Fig. S2** IRC calculation for acetylene hydrochlorination with (a) and without (b) TPPB catalyst.

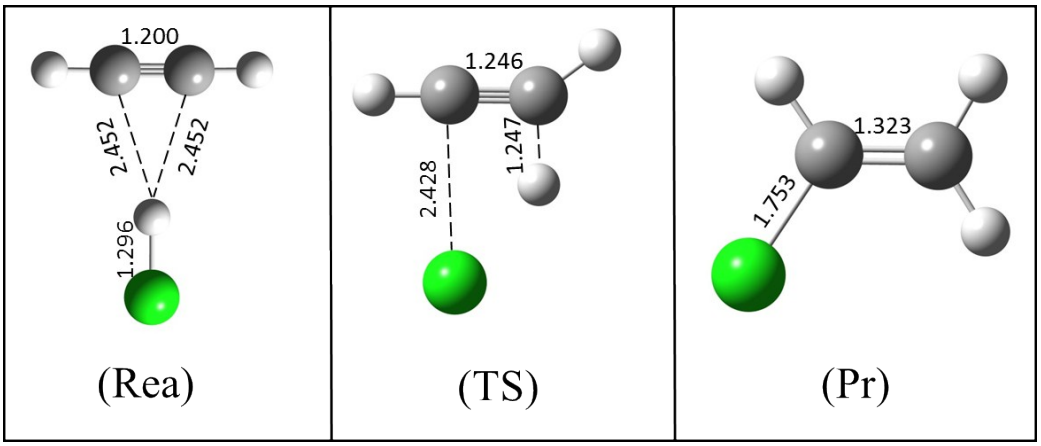


**Fig. S3** The geometries of the substances involved in the reaction pathway without catalyst. Carbon, hydrogen and chlorine atoms are depicted in gray, white and green, respectively.

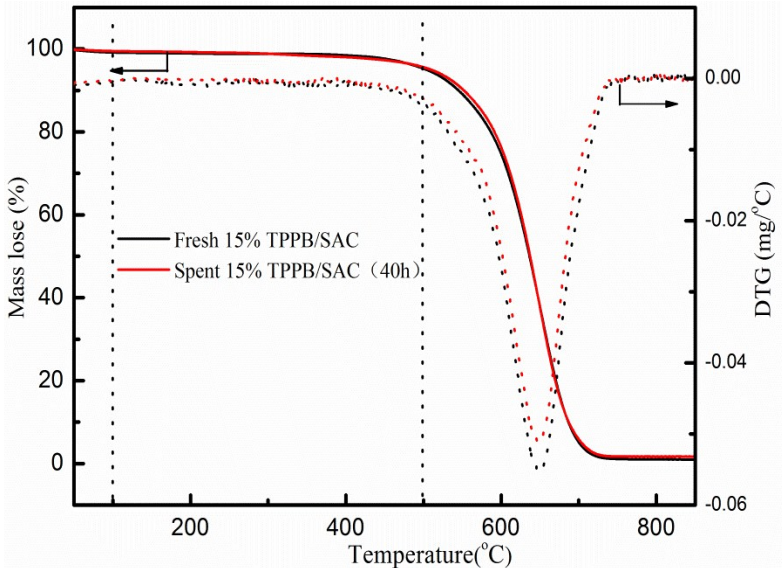


**Fig. S4** TGA curves of the fresh and spent 15% TPPB/SAC catalysts (after 40 h reaction, under the reaction conditions of 220 °C, GHSV ($C_2H_2$) = 30 $h^{-1}$ and $V_{HCl}/V_{C2H2}$ =1.15 ) in air atmosphere.