Synthesis of vinyl chloride monomer by acetylene hydrochlorination with a ruthenium-based N-heterocyclic carbene complex catalyst

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Supplementary Material

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Catalyst preparation

Preparation of imine

Firstly, 24.6 g of 2,6-diisopropylaniline and 100 mL of n-propanol were added to a 500-mL three-necked flask; then, 9.1 g of 40% aqueous glyoxal solution, 10 mL of n-propanol and 25 mL of deionized water were added into the former flask at room temperature. Condensing and refluxing the mixture at 70 °C with stirring for 1 h. After cooling, 100 mL of cold water was injected into thereto mixture. Finally, imine was obtained by filtration and desiccation at 60 °C.

Preparation of IPr salt

The mixture of 23.0 g of imine, 540 mL of ethyl acetate and 19 g of paraformaldehyde was added to a 100-mL round-bottom flask; next, the formed solution was heated and refluxed at 70 °C. And a solution of 7.65 mL trimethylchlorosilane dissolved in ethyl acetate was then added dropwise under stirring for 2 h. The solution was filtered three times with ethyl acetate, followed by vacuum drying at 40 °C overnight after it was cooled to 10 °C. The obtained sample was labelled as IPr salt.

Preparation of IPr (1, 3-bis (2, 6-diisopropylphenyl) imidazole-2-carbene)

8.4 g of IPr salt was dissolved in 110 mL anhydrous tetrahydrofuran in a 250-mL flask, and 1.6 g of potassium tert-butanol was added while stirring. The mixed solution was churned for another 30 min under nitrogen protection. Next, the solution was subjected to rotary evaporation, and after spinning, the residue was dissolved in 60 mL toluene at 60 °C. Subsequently, the filtrate was subjected to suction filtration through diatomaceous earth, followed by a second rotary distillation. The volume of the filtrate obtained by rotary evaporation was a quarter of that obtained by suction filtration, and the crystal precipitation could be observed. Finally, the produced solid was dried in a vacuum oven at 60 °C to yield the product.

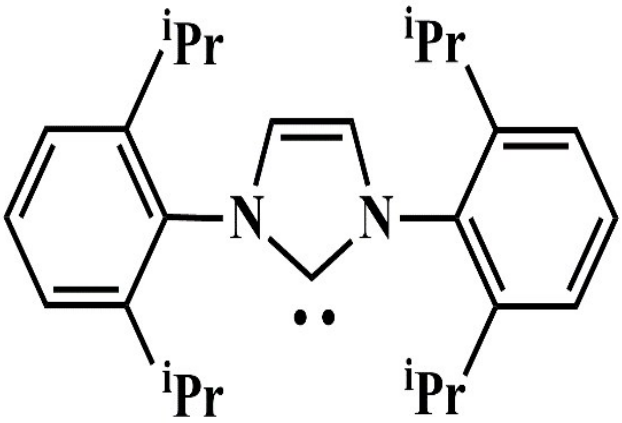


Fig. S1 The structure of N-heterocyclic carbene

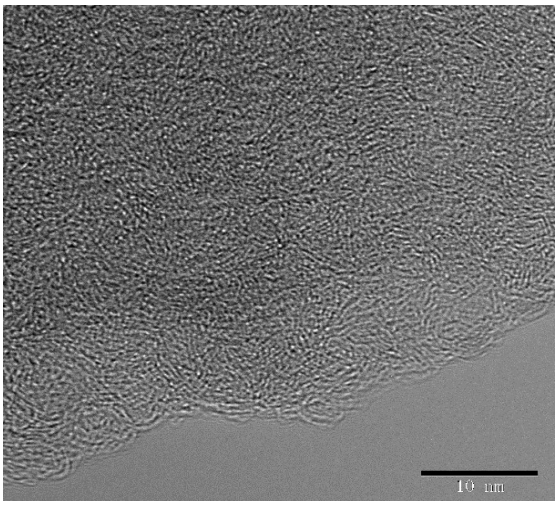


Fig. S2 TEM image of pure host AC

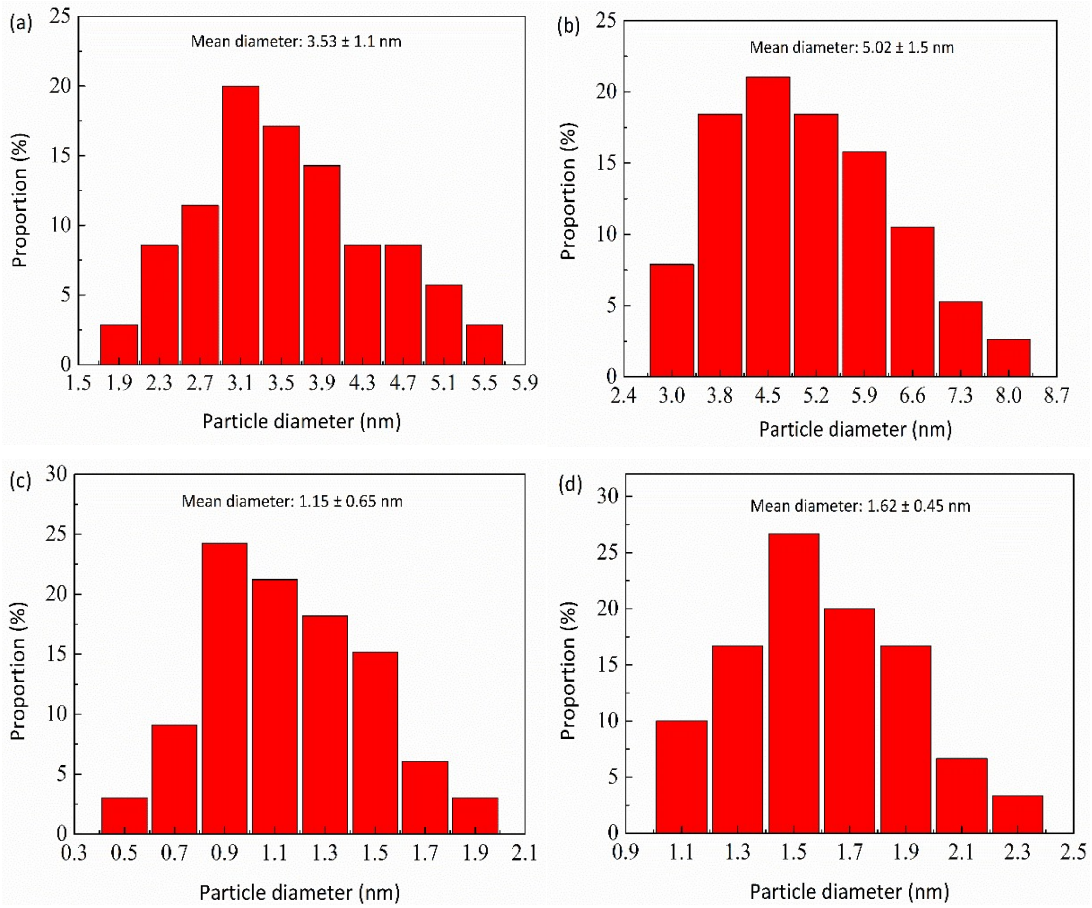
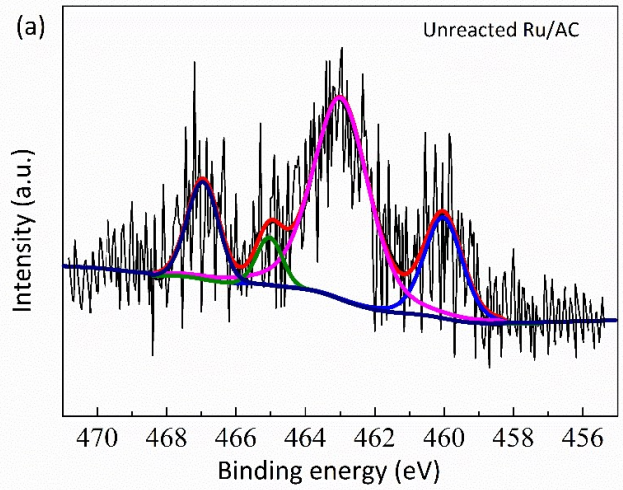
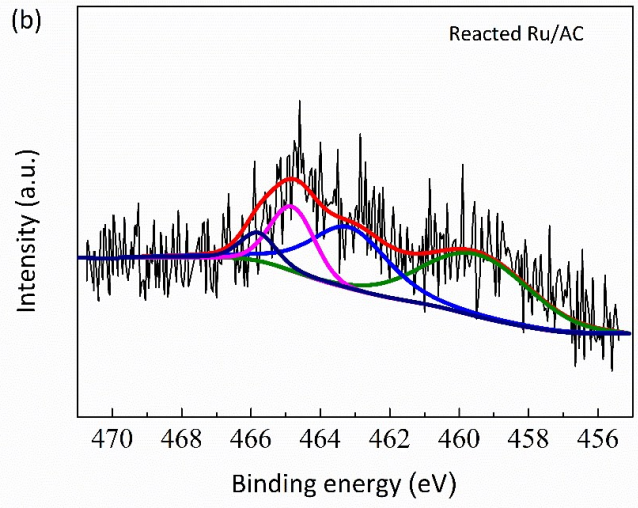
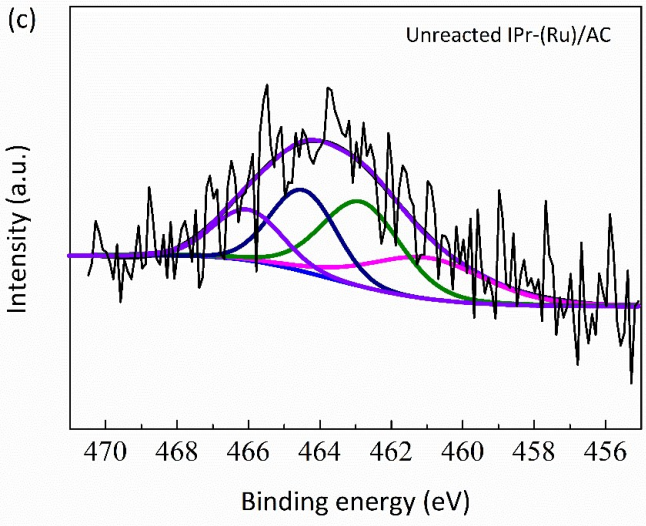


Fig. S3 Statistics of the particles size of the catalysts: (a) Unreacted Ru/AC, (b) Reacted Ru/AC, (c) Unreacted IPr-(Ru)/AC, and (d) Reacted IPr-(Ru)/AC; about 150 particles were measured for the unreacted and reacted samples


(a)
Unreacted Ru/AC
Intensity (a.u.)
470 468 466 464 462 460 458 456
Binding energy (eV)


(b)
Reacted Ru/AC
Intensity (a.u.)
470 468 466 464 462 460 458 456
Binding energy (eV)


(c)
Unreacted IPr-(Ru)/AC
Intensity (a.u.)
470 468 466 464 462 460 458 456
Binding energy (eV)

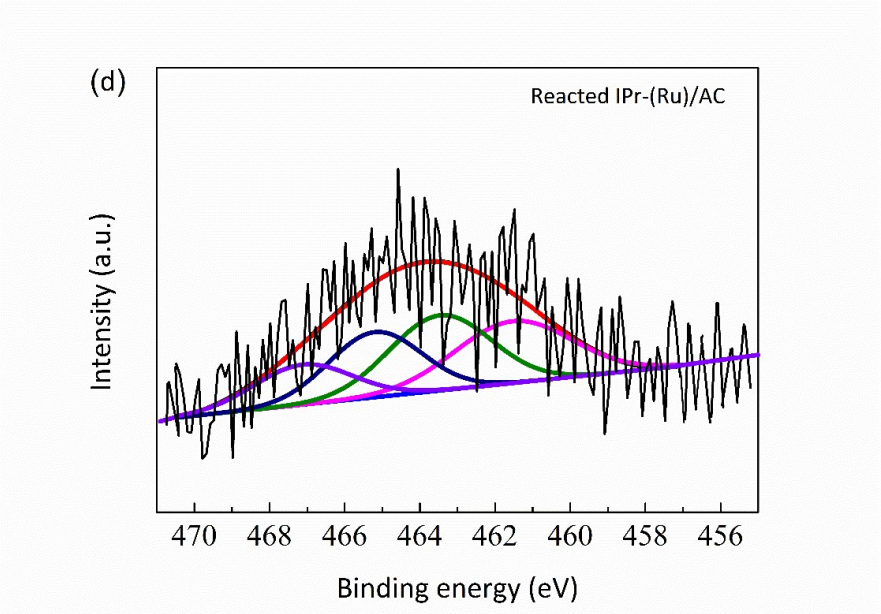


Fig. S4 High-resolution XPS spectra of Ru 3*p* of the unreacted and reacted catalysts

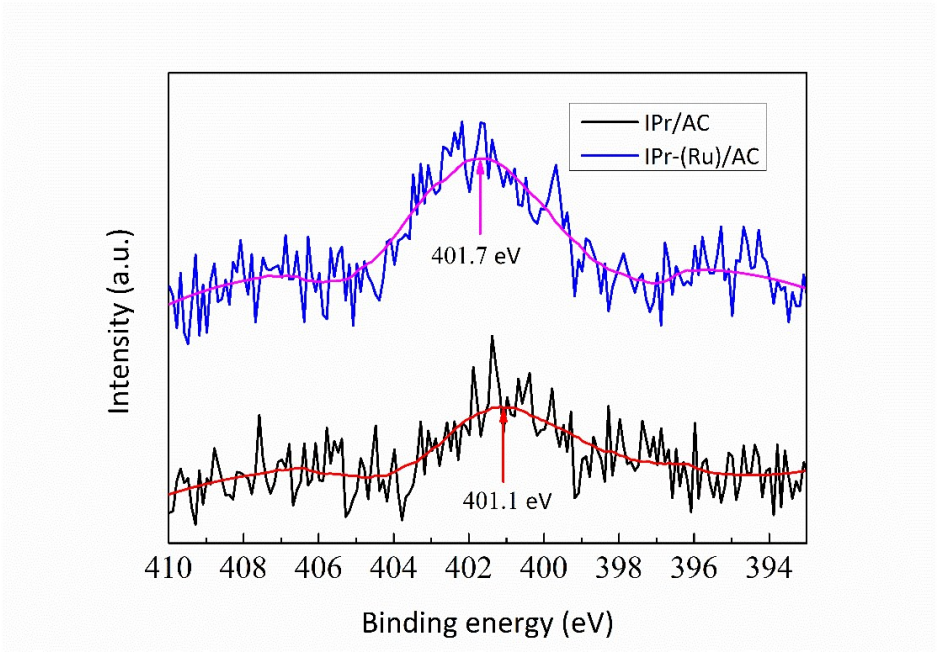


Fig. S5 N1*s* XPS spectra of the unreacted Ru-based catalysts

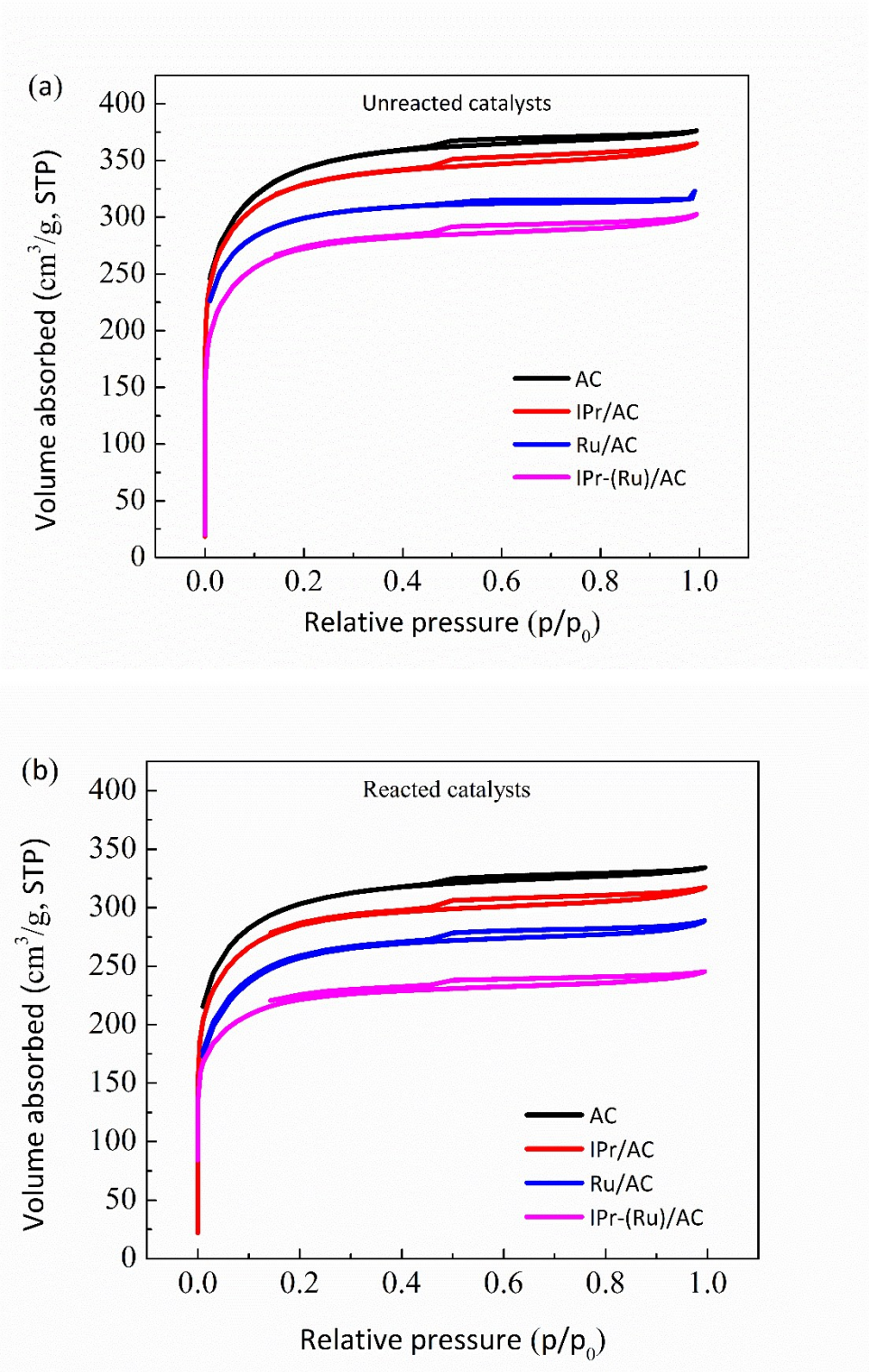


Fig. S6 Nitrogen adsorption-desorption isotherms of the unreacted (a) and reacted (b) catalysts

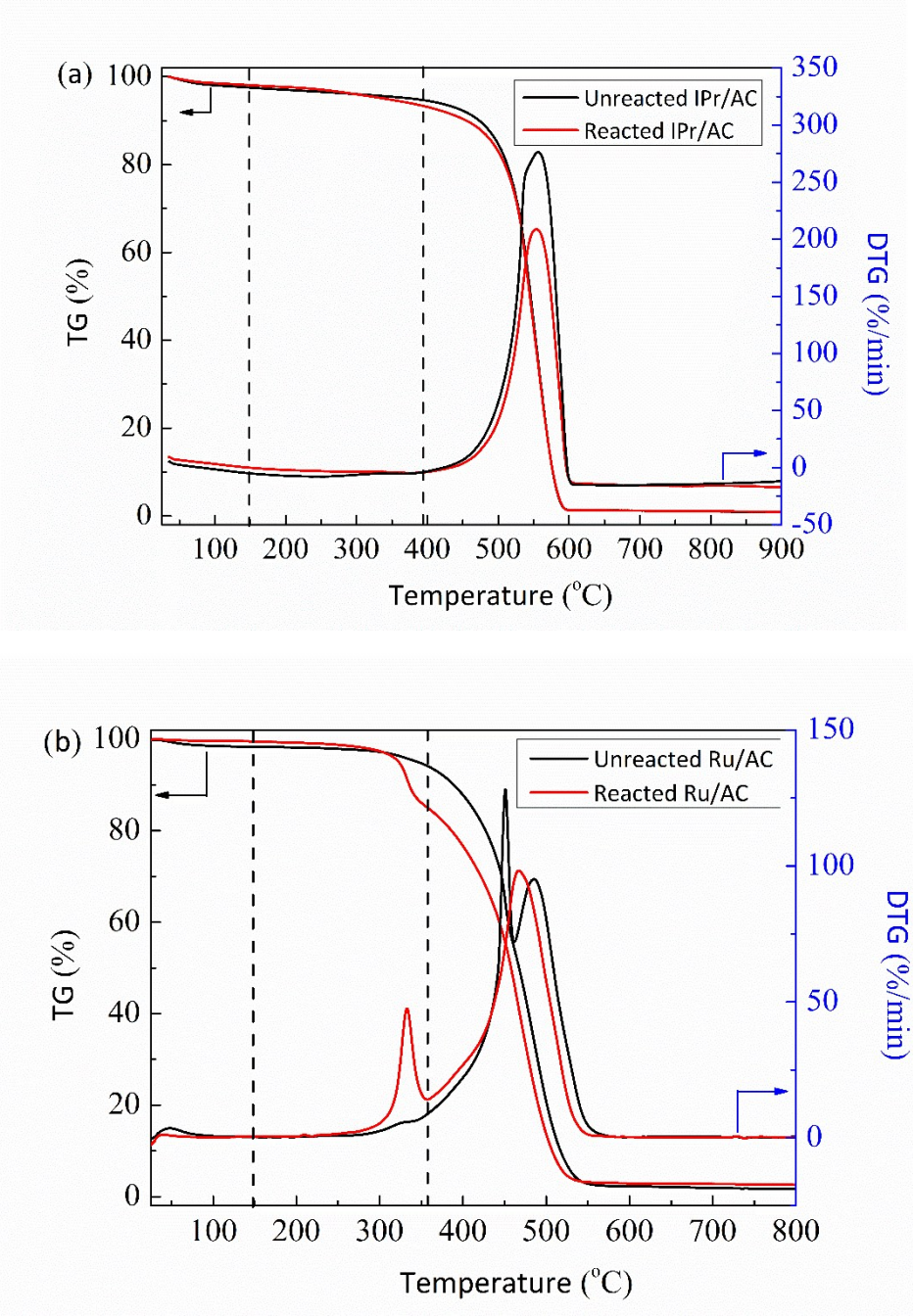


Fig. S7 TG curves of the unreacted and reacted catalysts recorded under air atmosphere