

Supplementary Material

Ionic Liquid-Solvent systems in gas-liquid phase reaction for acetylene hydrochlorination

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Table S1 Different combinations and catalytic performance of Ru salts, solvents and ionic liquids.

Catalysts	Ru mole concentration (mol/L)	TPPC mass fraction (%)	Solvents		Catalytic performance after 12h	
			Species	Mass fraction (%)	Acetylene conversion (%)	Selectivity of VCM (%)
Ru-GLY	0.0075	0	GLY	100	6.8	100
Ru-ISO	0.0075	0	ISO	100	3.2	100
Ru-PC	0.0075	0	PC	100	7.2	100
Ru-EC	0.0075	0	EC	100	0.8	95.0
Ru-TMS	0.0075	0	TMS	100	49.8	99.5
Ru-1TPPC-TMS	0.0075	1	TMS	99	90.2	99.5
Ru-5TPPC-TMS	0.0075	5	TMS	95	94.7	99.8
Ru-10TPPC-TMS	0.0075	10	TMS	90	95.5	99.8
Ru-15TPPC-TMS	0.0075	15	TMS	85	92.6	99.3
Ru-20TPPC-TMS	0.0075	20	TMS	80	92.8	99.5

Table S2 Prices of raw materials.

Material	CAS number	Pack Size	specification	Price /RMB	Manufacturer
[Bmim]Cl	79917-90-1	500 g	≥ 99%	800	D&B
[P ₄₄₄₄]Cl	2304-30-5	25 g	≥ 96%	263	D&B
[N ₄₄₄₄]Cl	1112-67-0	500 g	≥ 98%	589	D&B
TPPC	2001-45-8	100 g	≥ 98%	122	Meryer
NMPO	872-50-4	500 mL	≥ 99.5%	97	Macklin
TMS	126-33-0	500 mL	≥ 99%	43	Meryer

Table S3 The unit mass price and conversion of acetylene in Ru-ILs and Ru-10ILs-TMS system. Reaction conditions: $r(\text{RuCl}_3) = 0.0075 \text{ mol/L}$, $T=170^\circ\text{C}$, $\text{GHSV}(\text{C}_2\text{H}_2) = 50 \text{ h}^{-1}$, and $V(\text{HCl}) / V(\text{C}_2\text{H}_2) = 1.1$.

Catalyst	Unit mass price (RMB/g)	Conversion of acetylene (%)
Ru-[Bmim]Cl	1.6	66
Ru-10[Bmim]Cl-TMS	0.22	79.3
Ru-[P ₄₄₄₄]Cl	10.52	70
Ru-10[P ₄₄₄₄]Cl-TMS	1.11	92.4
Ru-[N ₄₄₄₄]Cl	1.18	60
Ru-10[N ₄₄₄₄]Cl-TMS	0.18	89.6
Ru-[Hnmpo]Cl	0.194	85
Ru-10[Hnmpo]Cl-TMS	0.08	85.9

Table S4 ICP-OES measurements of Ru-TPPC-TMS before and after the long-term reaction.

Ru content (mg/kg)	50 h ⁻¹		90 h ⁻¹	
	Fresh	Used	Fresh	Used
Nominal			501	
Actual	480.4	494.1	487.7	515.1

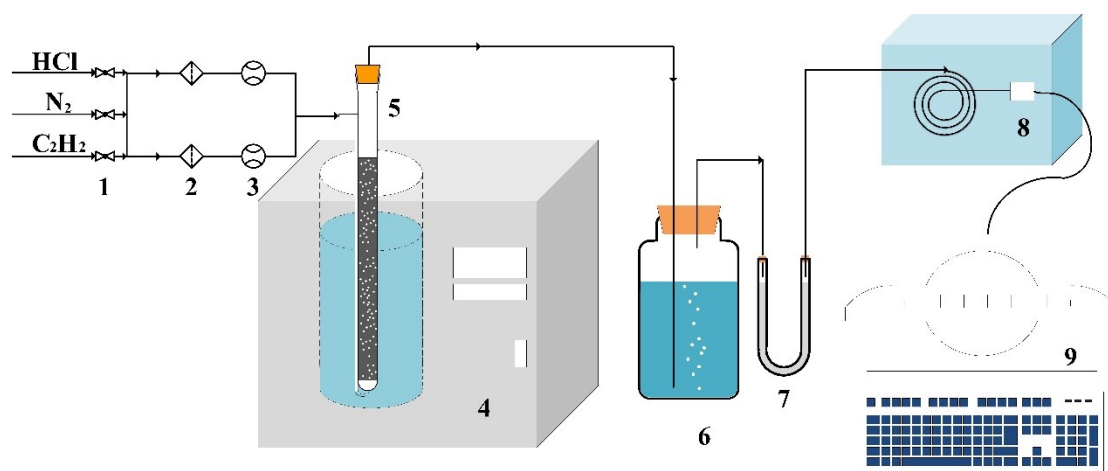
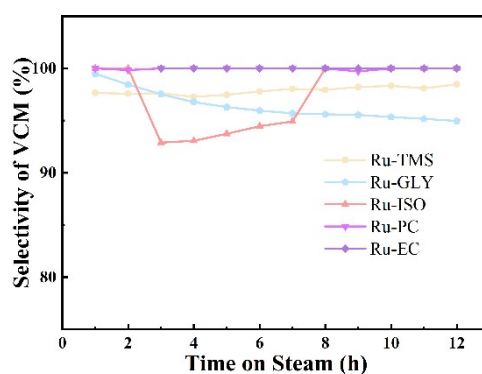


Figure S1 Experimental setup. 1-Pressure relief valve, 2-Filter, 3-Mass flowmeter, 4-Magnetic stirring oil bath, 5-Quartz bubbling micro-reactor, 6-Absorption bottle, 7-Drying tube, 8-Online GC, 9-PC.

Figure S2 Acetylene selectivity in acetylene hydrochlorination over different solvent systems.



Reaction conditions: $T = 170\text{ }^{\circ}\text{C}$, $\text{GHSV}(\text{C}_2\text{H}_2) = 50\text{ h}^{-1}$, and $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1.1$.

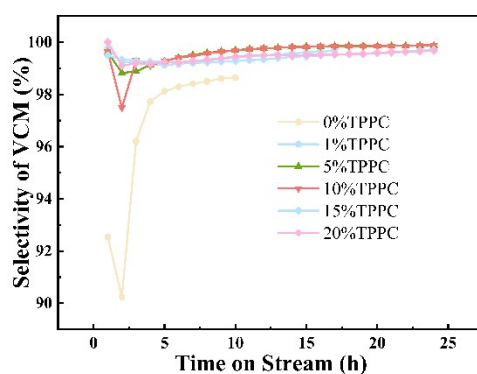


Figure S3 Acetylene selectivity in acetylene hydrochlorination over Ru-xTPPC-TMS. Reaction conditions: $T = 170\text{ }^{\circ}\text{C}$, $\text{GHSV}(\text{C}_2\text{H}_2) = 50\text{ h}^{-1}$, and $V(\text{HCl})/V(\text{C}_2\text{H}_2) = 1.1$.

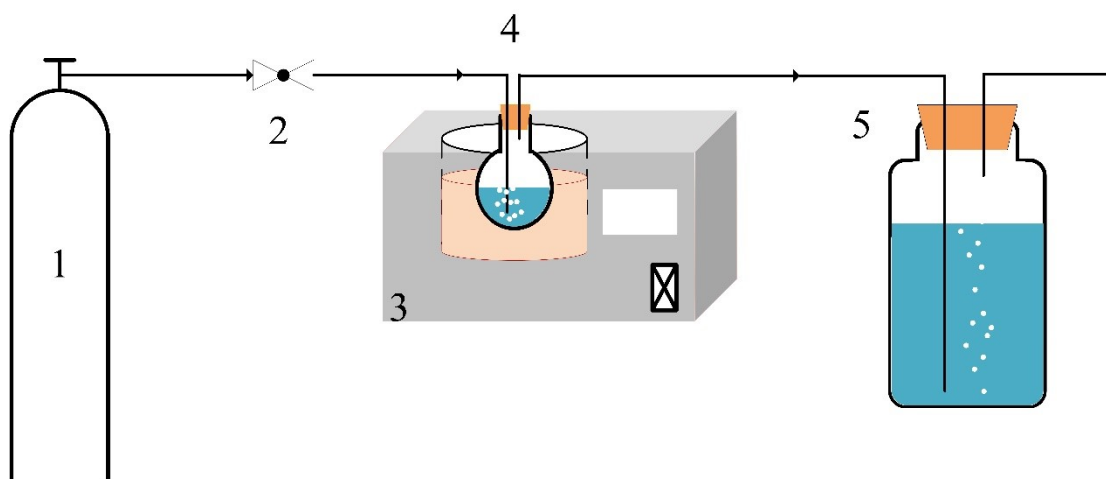


Figure S4 HCl/C₂H₂ adsorption capacity testing setup. 1-N₂/HCl/C₂H₂ gas, 2-valve, 3-constant temperature oil bath pot, 4-round bottom flask containing solvents, 5-NaOH adsorption solution.

The test of the adsorption capacity of solvents for HCl and C₂H₂ details: Firstly, N₂ was simultaneously introduced into the flask containing 40 mL solvent and then we detected the mass change at regular intervals by an electronic analytical balance with a precision of ± 0.1 mg. Then, HCl/C₂H₂ at the same gas rate was introduced into fresh solvent and the mass change was measured using the same method. The mass loss under the N₂ atmosphere is considered to be equal to the volatilization loss of solvent under the HCl/C₂H₂ atmosphere.

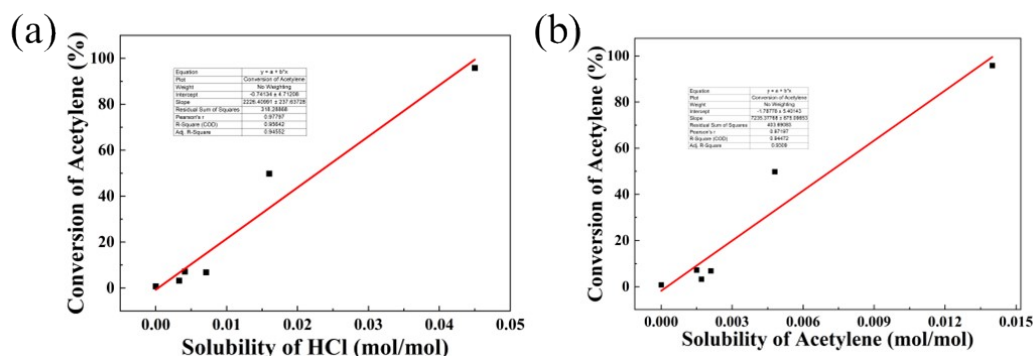


Figure S5 The solubility of the a) C₂H₂ and b) HCl vs the conversion of acetylene in different systems

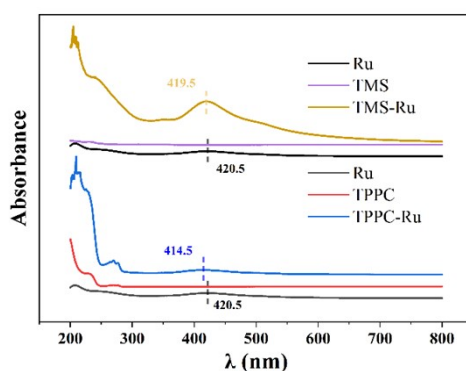


Figure S6 UV-vis absorption spectroscopy of Ru, TPPC, TMS, Ru-TPPC and Ru-TMS

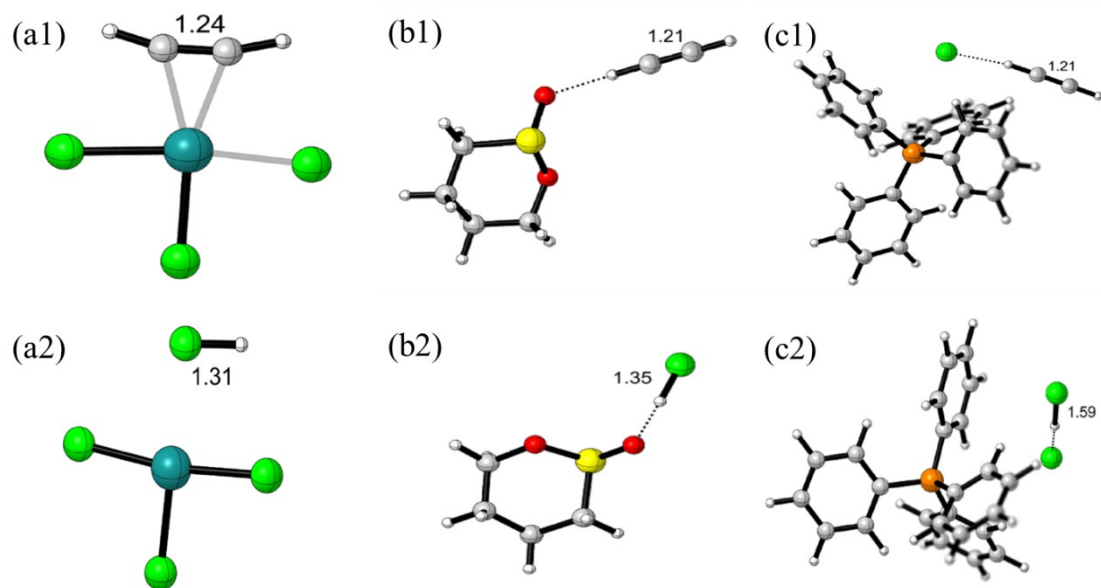


Figure S7 The absorption configurations of HCl and C₂H₂ on (a) RuCl₃, (b) TMS and (c) TPPC.

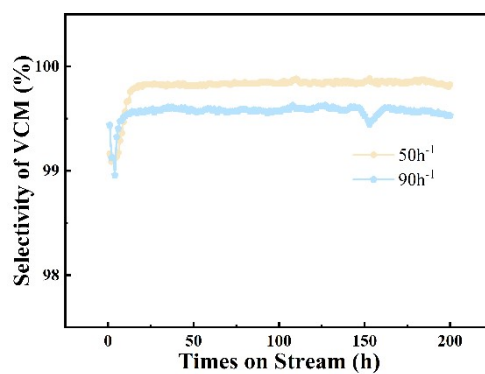


Figure S8 Acetylene selectivity in acetylene hydrochlorination of long-term stability of the Ru-10TPPC-TMS.

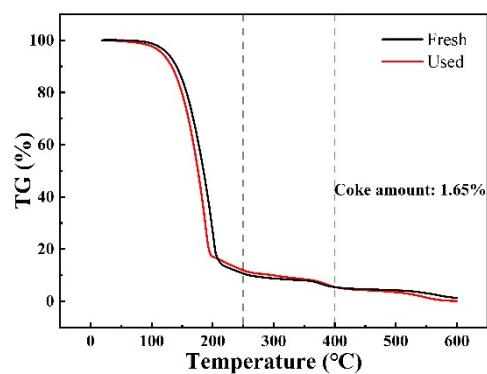


Figure S9 TGA curves of fresh and used Ru-TTPC-TMS after the long-term reaction in an air atmosphere.