On catalytic mechanism of [Bmim]Cl-transition metal catalysts for hydrochlorination of acetylene

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Table S1. Mulliken charge changes in adsorption configuration.

Table S2. HOMO and LUMO values and energy gaps of different substances.

Table S3. Mayer bond order of HCl on different catalysts.

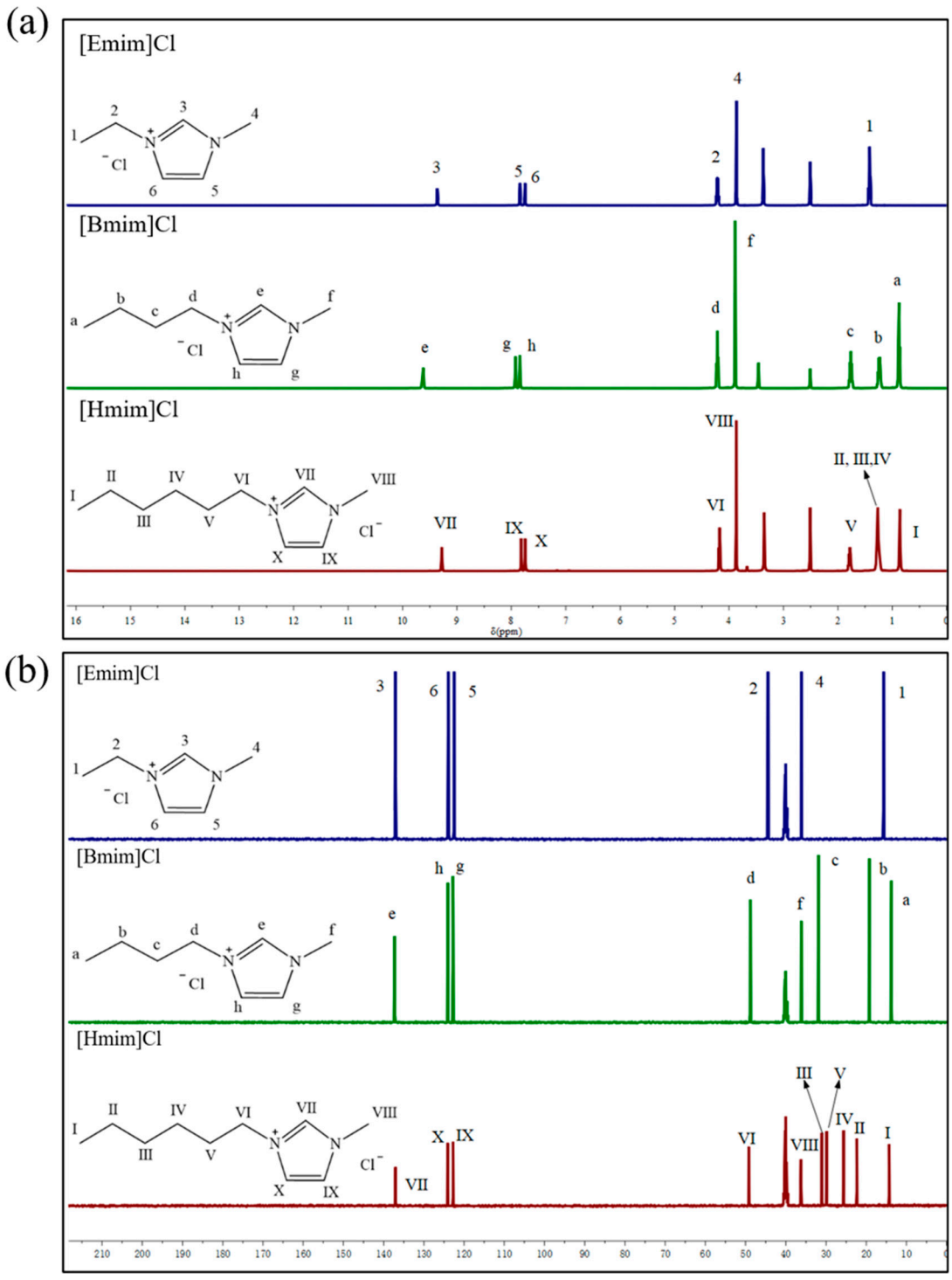
Table S4. Peak positions of IR spectra after catalysts absorbing C_2H_3Cl, C_2H_2, and HCl (cm^{-1}).

Table S5. Data for energy changes in ER mechanism for acetylene hydrochlorination. ($kcal \cdot mol^{-1}$)

Text S1. List of abbreviations to the manuscript.

Name	Abbreviation
Ionic liquids	ILs
Hydrogen chloride	HCl
Acetylene	C_2H_2
Vinyl chloride(C_2H_3Cl)	VCM
1-ethyl-3-methylimidazolium chloride	[Emim]Cl
1-butyl-3-methylimidazolium chloride	[Bmim]Cl
1-hexyl-3-methylimidazolium chloride	[Hmim]Cl
[Bmim]Cl-CuCl	B1
[Bmim]Cl-$CuCl_2$	B2
[Bmim]Cl-AgCl	B3
[Bmim]Cl-$RuCl_3$	B4
Density functional theory	DFT
Electrostatic potential	ESP
Highest occupied molecular orbital	HOMO
Lowest unoccupied molecular orbital	LUMO
Transition state	TS
Intermediate product	INT
Electron localization function	ELF
Partial density of states	PDOS
Intrinsic reaction coordinates	IRC

Text S2. ^{1}H NMR and ^{13}C NMR analysis of ionic liquids. (DMSO-d_6: 2.5 ppm in ^{1}H NMR and 39.53±0.05 ppm in ^{13}C NMR, water 3.33 ppm in ^{1}H NMR)



(a) ^{1}H NMR (500 MHz, DMSO). **[Emim]Cl**: δ 9.28 (s, 13H), 7.82 (s, 13H), 7.73 (d, J = 17.7 Hz, 13H), 4.18 (t, J = 7.2 Hz, 26H), 4.02 (d, J = 10.1 Hz, 1H), 3.87 (s, 38H), 3.67 (s, 1H), 3.35 (s, 30H), 2.51 (s, 30H), 1.88 – 1.68 (m, 27H), 1.50 (s, 1H), 1.41 – 1.36 (m, 1H), 1.27 (s, 83H), 0.86 (t, J = 6.7 Hz, 40H). **[Bmim]Cl**: δ 9.28 (s, 13H), 7.82 (s, 13H), 7.73 (d, J = 17.7 Hz, 13H), 4.18 (t, J = 7.2 Hz,

26H), 4.02 (d, J = 10.1 Hz, 1H), 3.87 (s, 38H), 3.67 (s, 1H), 3.35 (s, 30H), 2.51 (s, 30H), 1.88 – 1.68 (m, 27H), 1.50 (s, 1H), 1.41 – 1.36 (m, 1H), 1.27 (s, 83H), 0.86 (t, J = 6.7 Hz, 40H). **[Hmim]Cl**: δ 9.28 (s, 13H), 7.82 (s, 13H), 7.73 (d, J = 17.7 Hz, 13H), 4.18 (t, J = 7.2 Hz, 26H), 4.02 (d, J = 10.1 Hz, 1H), 3.87 (s, 38H), 3.67 (s, 1H), 3.35 (s, 30H), 2.51 (s, 30H), 1.88 – 1.68 (m, 27H), 1.50 (s, 1H), 1.41 – 1.36 (m, 1H), 1.27 (s, 83H), 0.86 (t, J = 6.7 Hz, 40H).

(b) ^{13}C NMR (126 MHz, DMSO). **[Emim]Cl**: δ 137.03 (s), 123.94 (s), 123.69 (s), 122.47 (s), 44.44 (s), 41.54 – 40.15 (m), 40.02 (s), 39.85 (s), 39.68 (s), 39.52 (s), 36.10 (s), 15.70 (s). **[Bmim]Cl**: δ 137.25 (s), 124.02 (s), 122.75 (s), 48.82 (s), 41.19 – 40.17 (m), 40.02 (s), 39.85 (s), 39.69 (s), 39.52 (s), 36.15 (s), 31.87 (s), 19.22 (s), 13.74 (s). **[Hmim]Cl**: δ 137.04 (s), 124.07 (s), 122.73 (s), 49.20 (s), 40.79 – 39.92 (m), 39.84 (s), 39.68 (s), 39.51 (s), 36.22 (s), 31.02 (s), 29.82 (s), 25.61 (s), 22.35 (s), 14.32 (s).

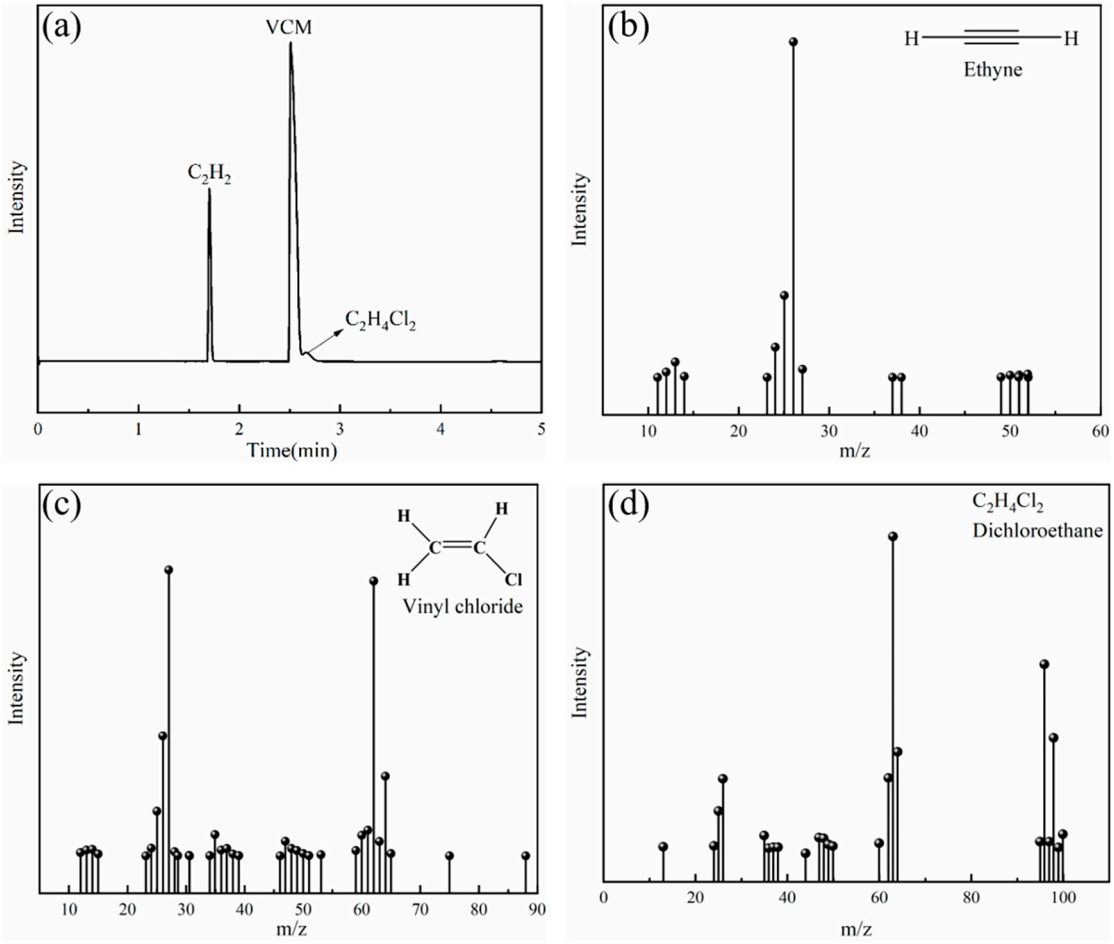


Figure S1. Gas chromatograms (a) and mass spectra (b-d) of the gases after the reaction.

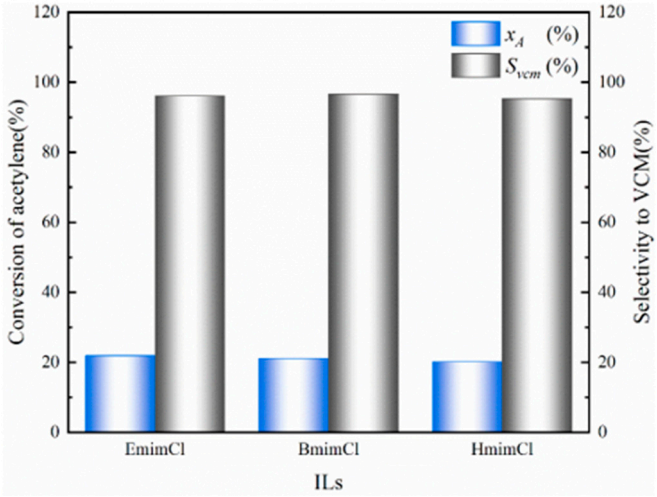


Figure S2. Acetylene conversion and vinyl chloride selectivity by ILs at the fixed reaction condition (160 °C, n_{HCl}/n_{C2H2} = 1~1.2, 1 h).

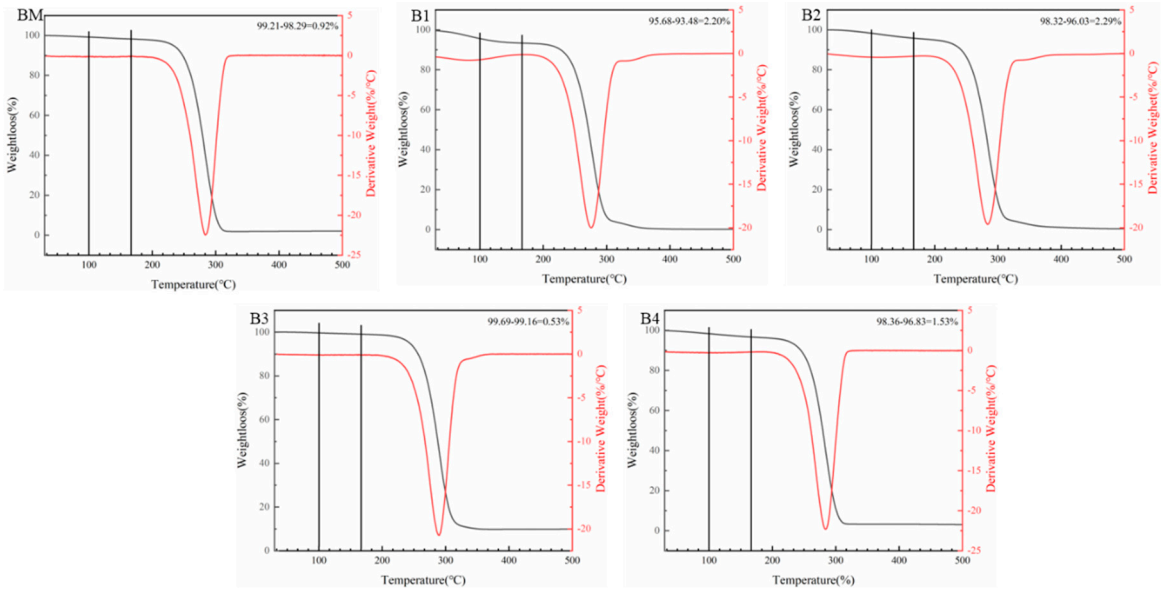


Figure S3. TG curves of different IL-based catalysts.

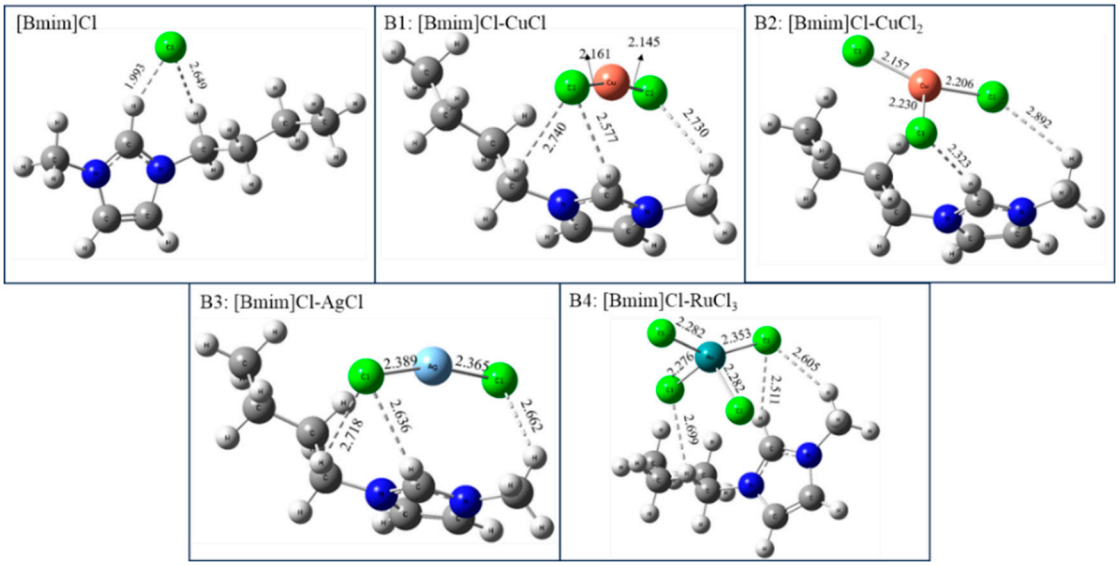


Figure S4. Structure of five IL-based Catalysts.

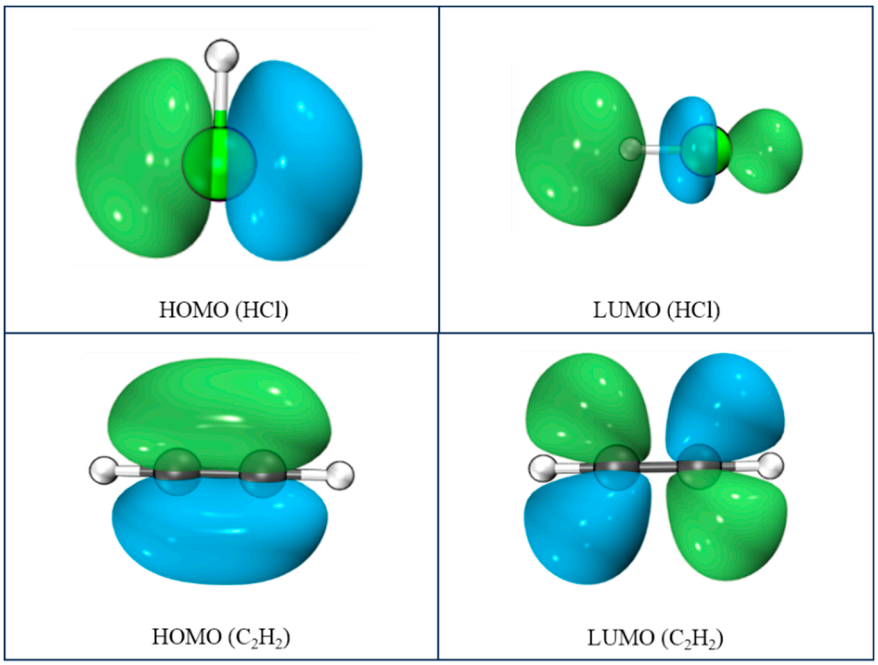


Figure S5. HOMO/LUMO orbitals of HCl and C_2H_2.

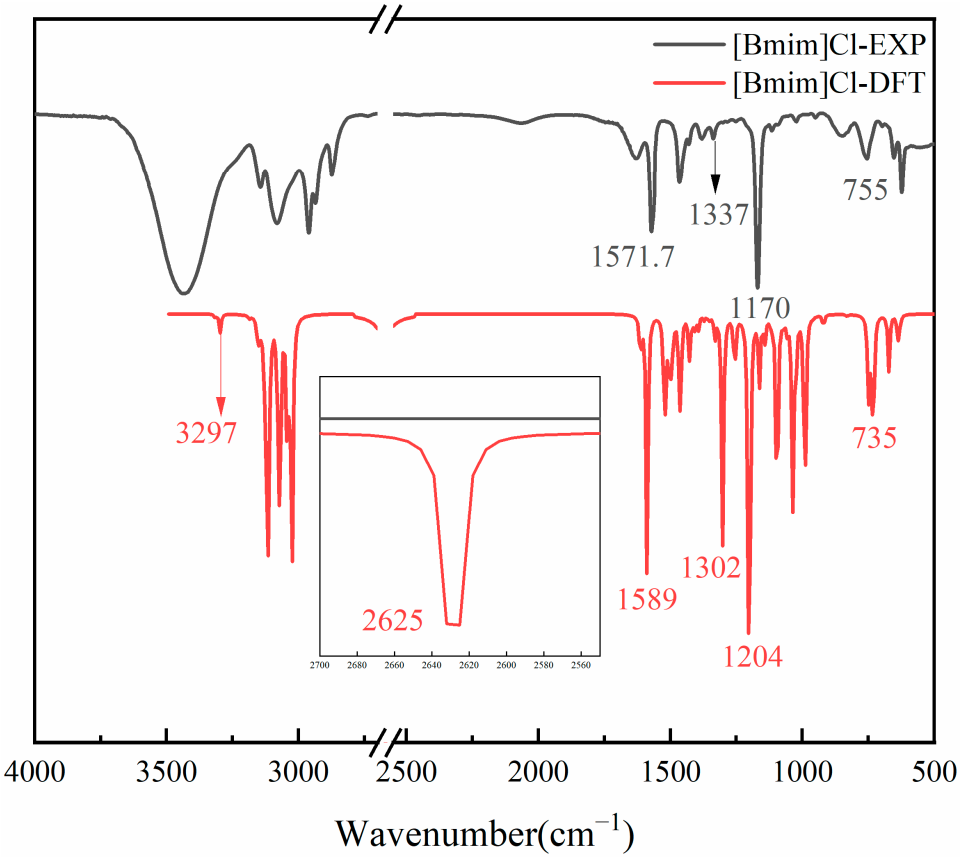


Figure S6. Comparison between the IR experiment spectrum and the DFT simulation spectrum of [Bmim]Cl.

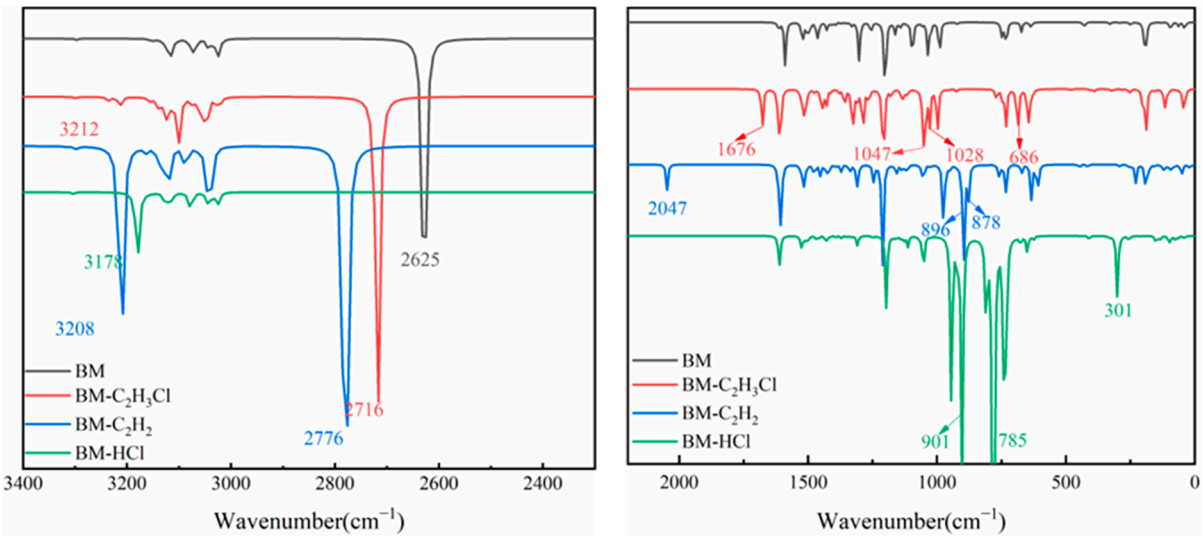


Figure S7. Simulated IR spectra of [Bmim]Cl in presence of C_2H_2, HCl, and VCM.

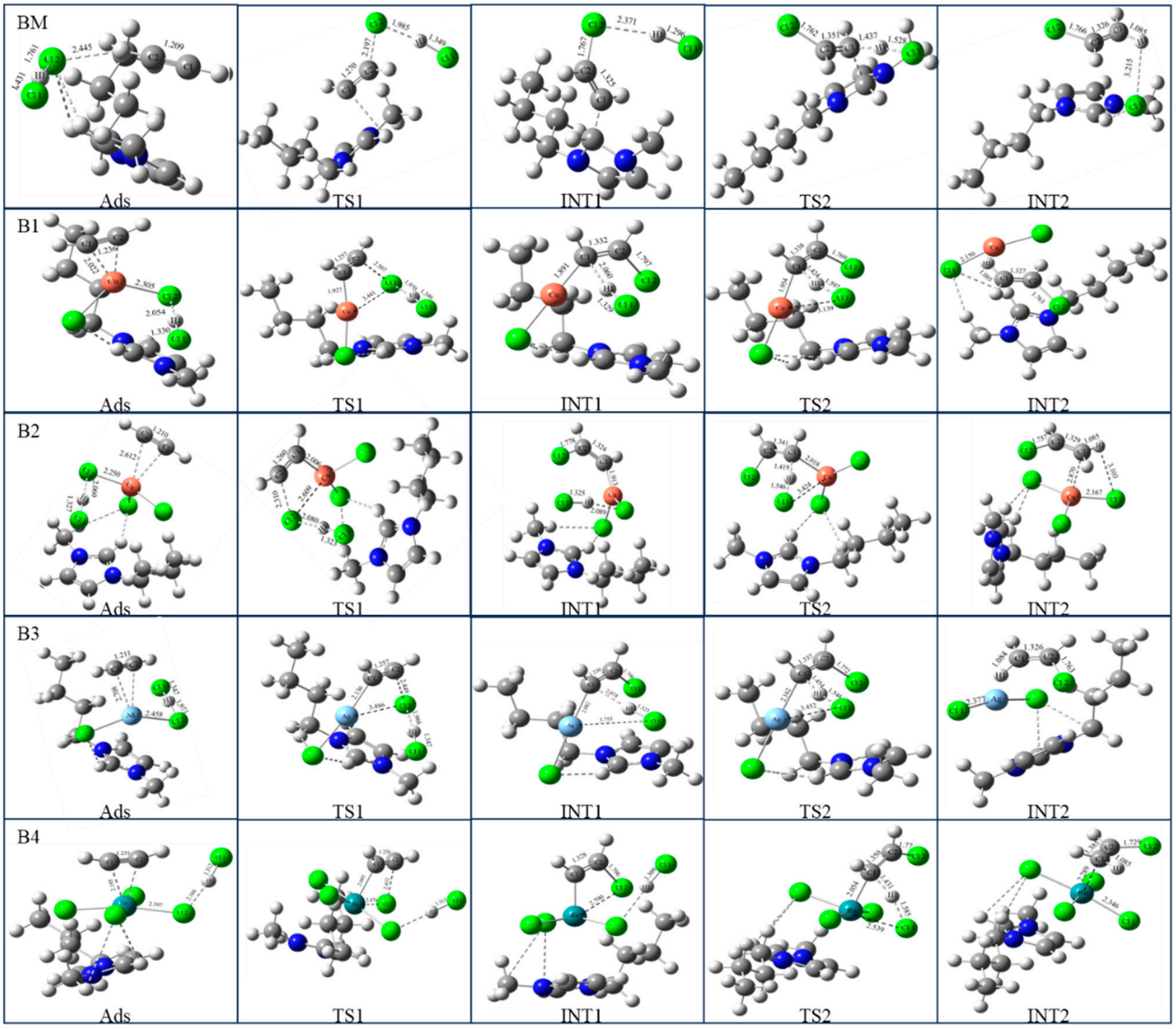


Figure S8. Configuration details during catalytic process.

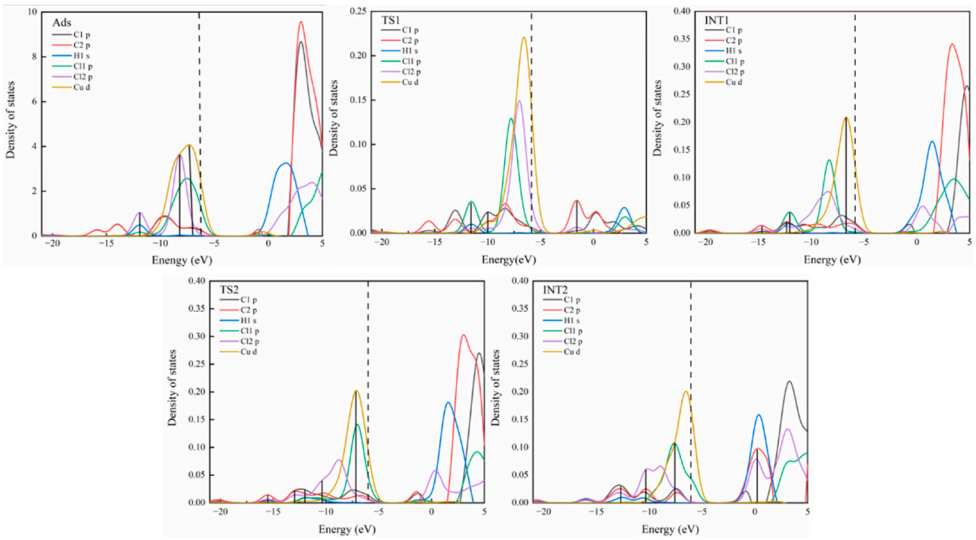


Figure S9. PDOS of the catalytic reaction process on B1.

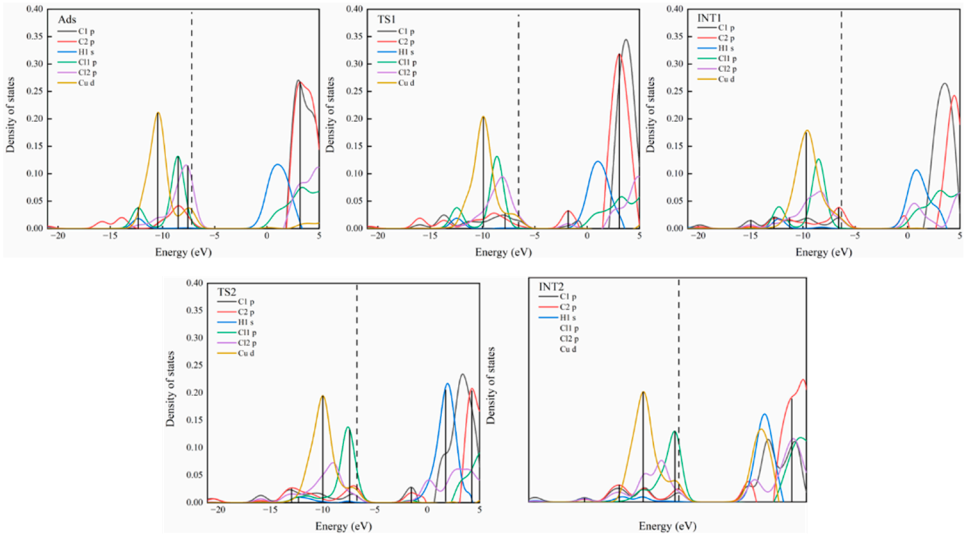


Figure S10. PDOS of the catalytic reaction process on B2.

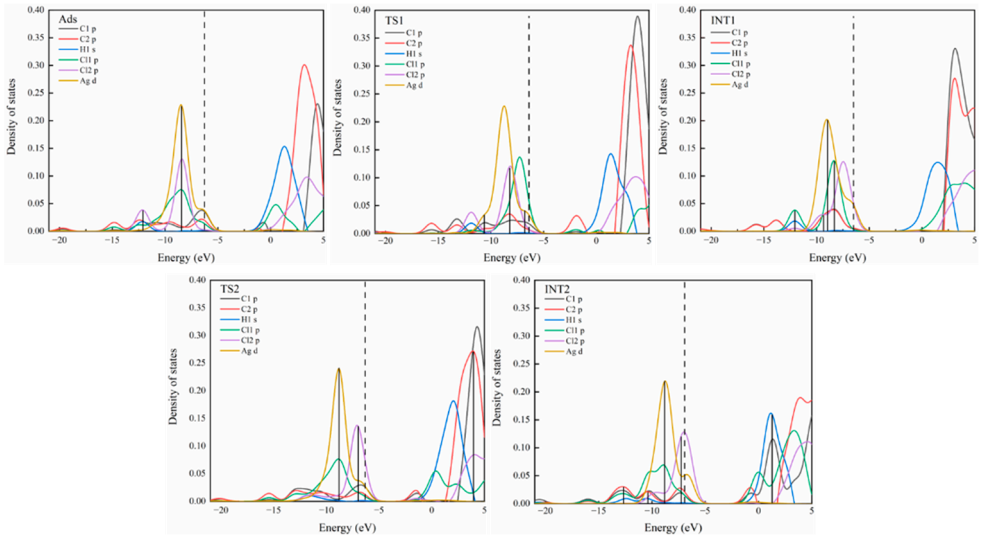


Figure S11. PDOS of the catalytic reaction process on B3.

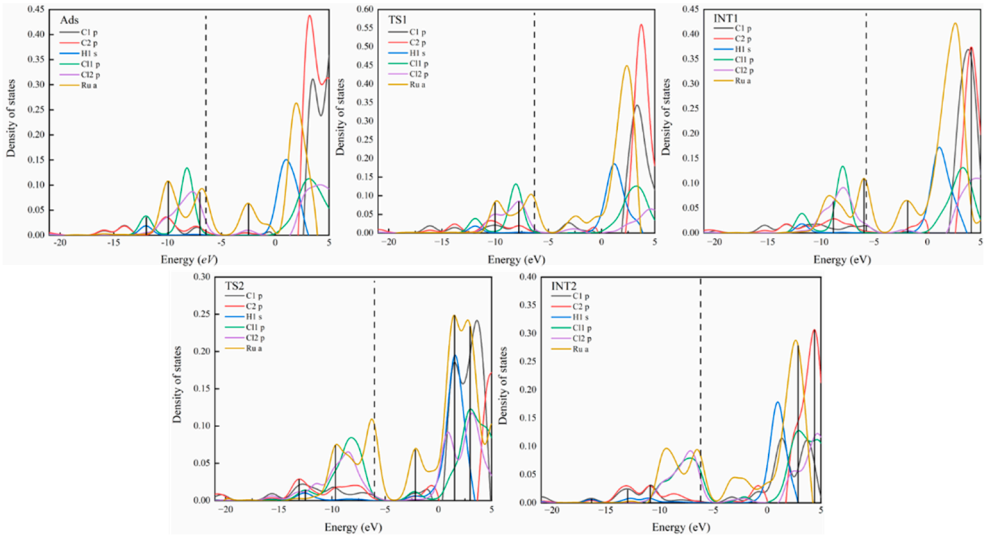


Figure S12. PDOS of the catalytic reaction process on B4.

Table S1. Mulliken charge changes in adsorption configuration.

Configuration	BM	B1	B2	B3	B4
Adsorption of HCl	−0.322	−0.105	−0.07	−0.129	−0.059
Adsorption of C_2H_2	−0.032	+0.019	+0.014	+0.001	+0.017
Adsorption of C_2H_3Cl	−0.029	+0.018	+0.011	+0.025	0

("-" means gaining electrons, "+" means losing electrons).

Table S2. HOMO and LUMO values and energy gaps of different substances.

substance	Eigenvalues (eV)		Energy gaps (eV)			
	HOMO	LUMO	$LUMO_{(HCl)}$–$HOMO_{(IL)}$	$LUMO_{(C2H2)}$–$HOMO_{(IL)}$	$LUMO_{(IL)}$–$HOMO_{(HCl)}$	$LUMO_{(IL)}$–$HOMO_{(C2H2)}$
[Bmim]Cl	−5.38	−1.18	4.63	6.76	8.03	6.50
B1	−5.93	−1.55	5.18	7.31	7.66	6.13
B2	−7.05	−1.56	6.30	8.43	7.65	6.12
B3	−6.42	−1.61	5.67	7.80	7.60	6.07
B4	−6.00	−3.25	5.25	7.38	5.96	4.43
HCl	−9.21	−0.75				
C_2H_2	−7.68	1.38				

Table S3. Mayer bond order of HCl on different catalysts.

ILs	Mayer bond order of HCl
HCl	0.9943
BM	0.5394
B1	0.8433

B2	0.8849
B3	0.8134
B4	0.8626

Table S4. Peak positions of IR spectra after catalysts absorbing C_2H_3Cl, C_2H_2, and HCl (cm^{-1}).

ILs	BM	B1	B2	B3	B4
C-H on imidazole ring (*V*)	2625	3269	3188	3268	3262
ILs-C_2H_3Cl	BM	B1	B2	B3	B4
C-H on imidazole ring (*V*)	2716	3253	3212	3324	3316
C-H (*V*)	3212	3220	3180	3300	3220
C-H (γ)	1052	1004/943	996	994	1012/932
C-H (β)	1028	1044	1028	1028	1044
C-H (δ)	1676	1676	1676	1676	1684
C-Cl (*V*)	686	692	692	684	692
ILs-C_2H_2	BM	B1	B2	B3	B4
C-H on imidazole ring (*V*)	2776	3307	3379	3325	3280
C-H $(V^a)^s$	3208	3343	3217	3398	3397
C-H (V^s)	2047	2065	2074	2065	2074
C-H (β)	896	850	832	868	823
C-H (γ)	878	823	814	850	814
ILs-HCl	BM	B1	B2	B3	B4
C-H on imidazole ring (*V*)	3178	3276	3300	3311	3276
H-Cl (*V*)	301	2409	2508	2170	2596

H-Cl (ω)	901	572	540	651	500
H-Cl (ρ)	785	540	492	629	445

Table S5. Data for energy changes in ER mechanism for acetylene hydrochlorination. (kcal·mol^{-1})

Catalyst	[Bmim]Cl	[Bmim]Cl-CuCl (B1)	[Bmim]Cl-$CuCl_2$ (B2)	[Bmim]Cl-AgCl (B3)	[Bmim]Cl-$RuCl_3$ (B4)
Cat	0.00	0.00	0.00	0.00	0.00
Ads	−7.87	−2.91	−2.11	−1.11	−9.49
TS1	32.45	24.60	22.45	22.00	5.78
INT1	6.09	13.70	6.74	11.57	−9.95
TS2	23.66	15.88	14.24	15.20	0.17
INT2	−20.23	−18.35	−16.90	−20.05	−25.14
Cat+VCM	−21.09	−21.09	−21.09	−21.09	−21.09