Supplementary Material

A study on the rules of ligands in highly efficient Ru-amide/AC catalysts for acetylene hydrochlorination

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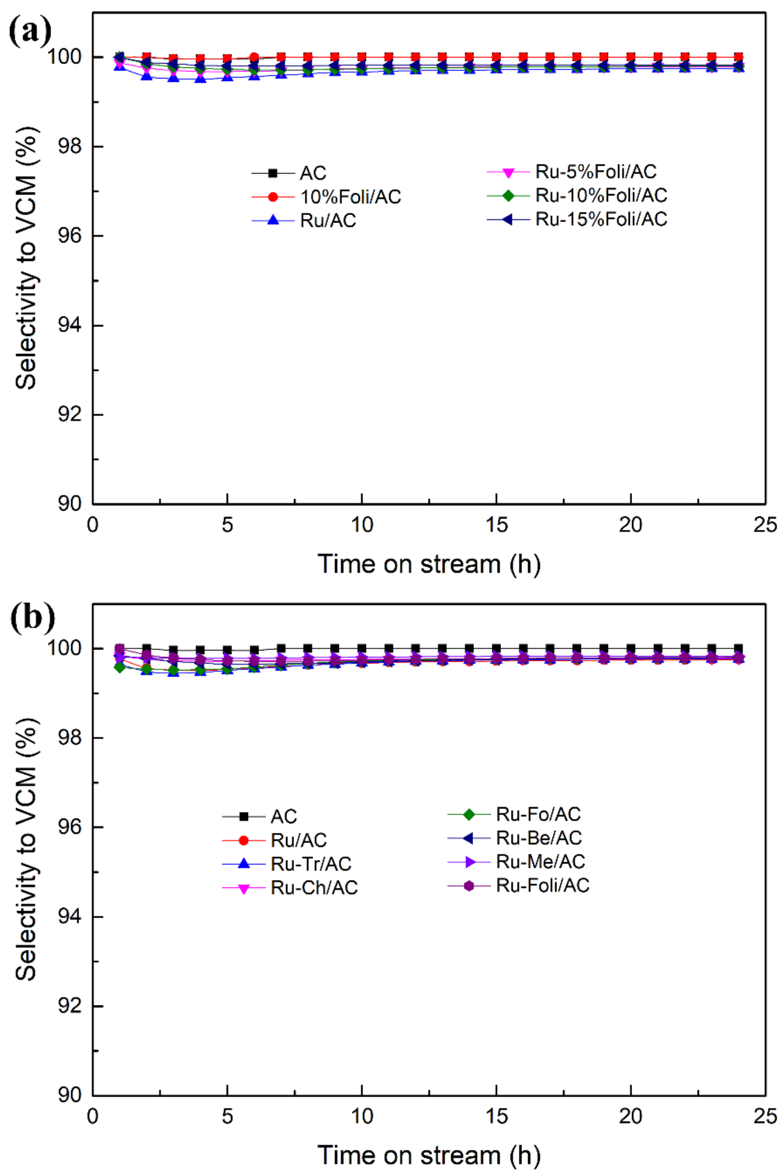


Fig. S1. VCM selectivity in acetylene hydrochlorination over (a) Ru-Foli/AC catalysts and (b) Ru-amide/AC catalysts. Reaction conditions: T = 150 °C, GHSV(C_2H_2) = 360 h^{-1}, and $V_{HCl}/V_{C_2H_2}$ = 1.15.

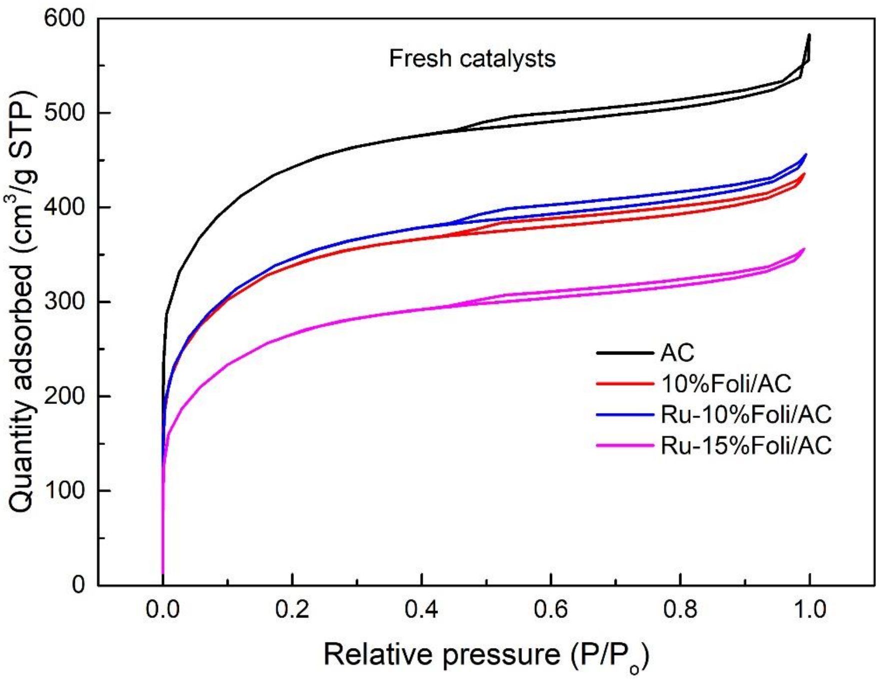


Fig. S2. N_2 adsorption-desorption isotherms of fresh catalysts

Table S1 The texture properties of fresh catalysts

Catalysts	S_{BET} ($m^2 \cdot g^{-1}$)	V_P^d ($cm^3 \cdot g^{-1}$)
AC	1435.6	0.90
10%Foli/AC	1123.5	0.67
Ru-10%Foli/AC	1138.6	0.71
Ru-15%Foli/AC	897.48	0.55

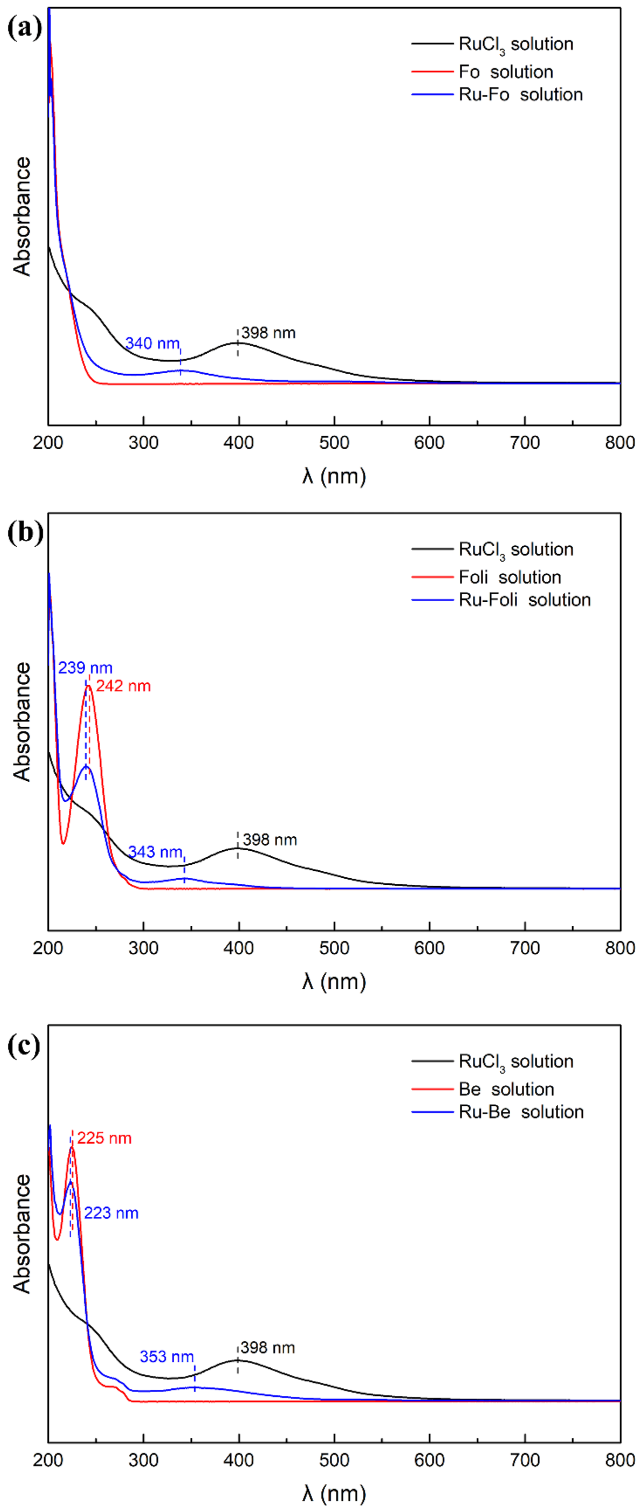


Fig. S3. UV-vis absorption spectroscopy of Ru, amide ligands, and Ru-amide ligands solution.

The UV-vis absorption spectroscopy of $RuCl_3$ solution shows a peak at 398 nm which corresponds to *d*-*d* transition of Ru^{n+}. As can be seen from Fig. S3(a), formamide shows no peak, while an absorption peak at 340 nm appears in the spectrum of Ru-Fo solution, which is the blue shift of the Ru^{n+} peak. In Fig. S3(b), there is an absorption peak at 242 nm in the spectrum of formanilide, which shifts to 239 nm in the spectrum of Ru-Foli solution. Besides, the absorption peak of Ru^{n+} in Ru-Foli solution also shifted to 343 nm. As for Fig. S3(c), same to Fig. S3(b), the absorption peaks of benzamide (from 225 to 223 nm) and Ru^{n+} (from 398 to 353 nm) are blue-shifting. Because of the complexation between Ru^{n+} and amide ligands, the charge transition requires more energy so that the absorption peak moves to the short wavelength.

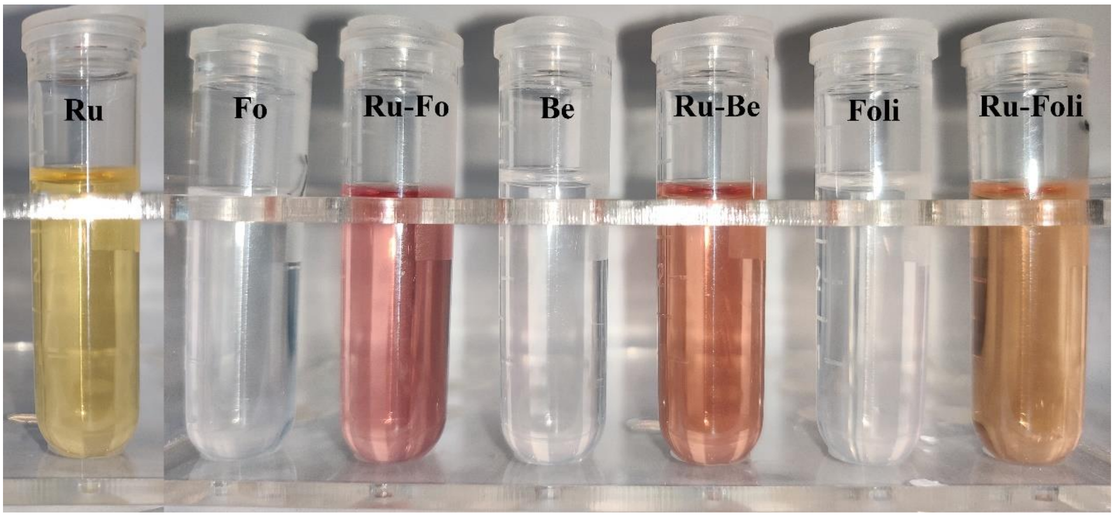


Fig. S4. Solutions of different samples.

$RuCl_3$ and amide ligands were dissolved in ethanol respectively, and Ru-amide solutions with the same ruthenium concentration as Ru solution were configured. It can be seen from Fig. S4 that the colors of Ru-amide solutions have changed compared with Ru solution, and the ligands themselves are colorless, which proves that the ligands may interact with ruthenium.

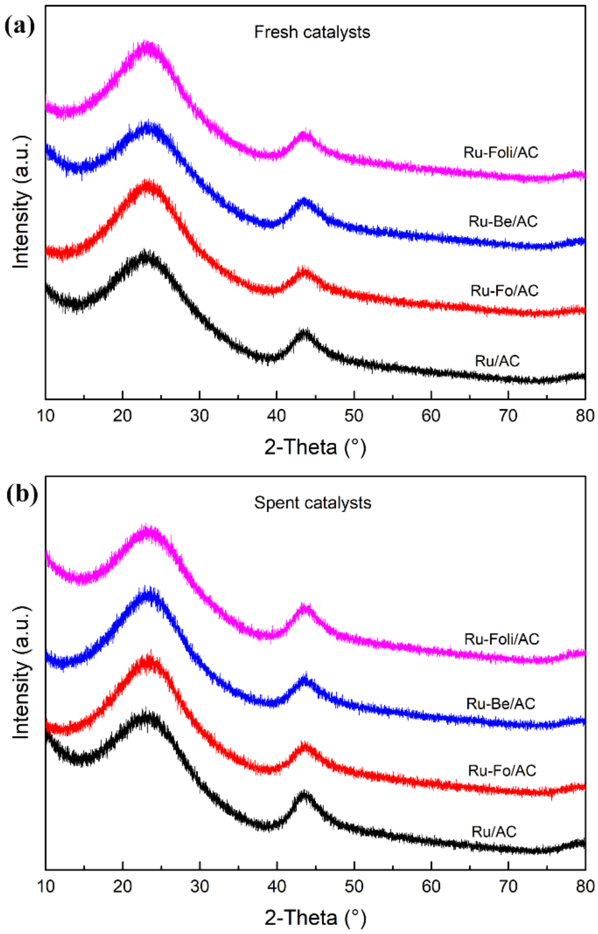


Fig. S5. XRD patterns of fresh and spent Ru-based catalysts.

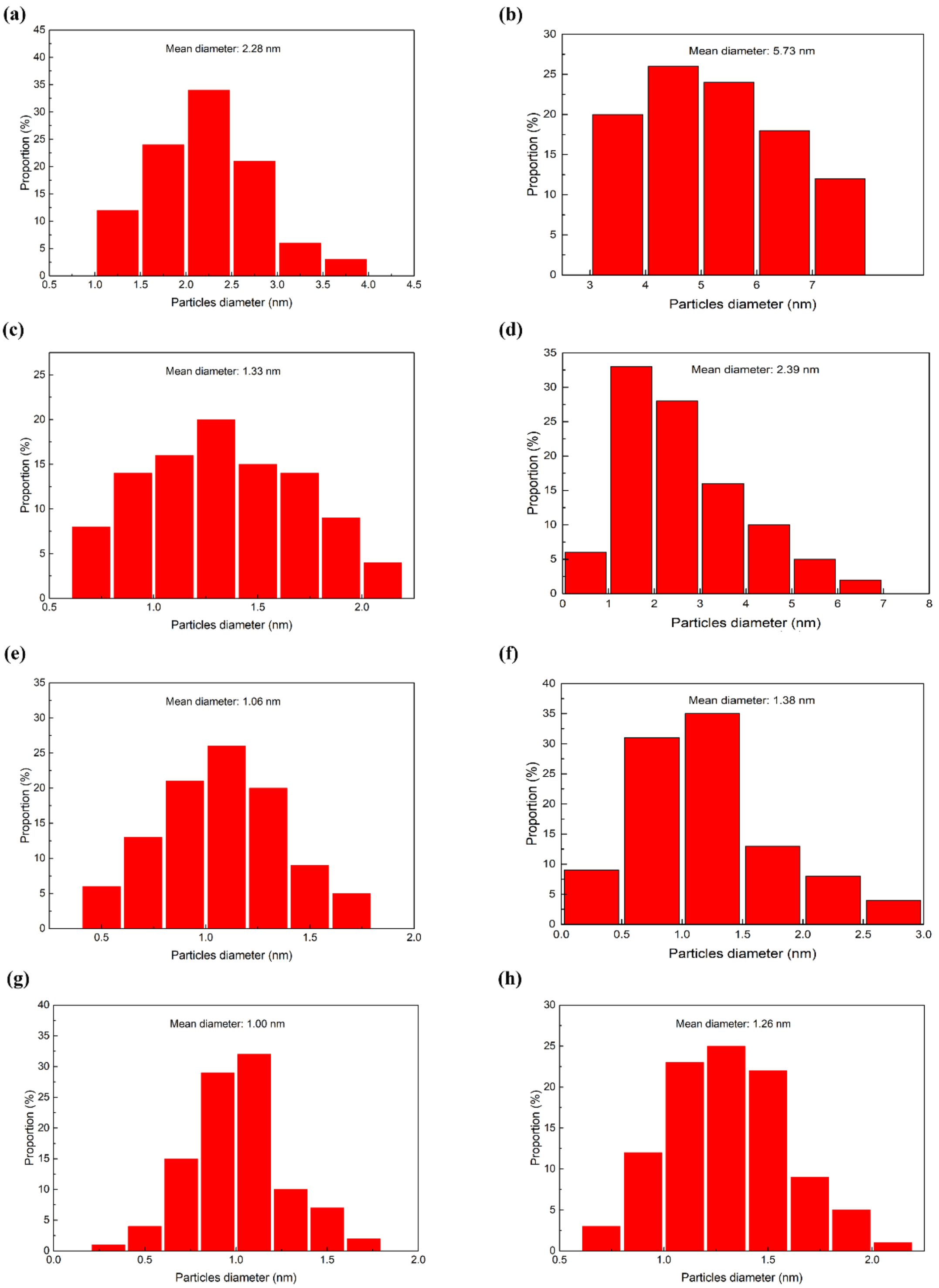


Fig. S6. Statistical data of particle size distribution of fresh and spent catalysts: (a) Fresh Ru/AC, (b) Spent Ru/AC, (c) Fresh Ru-Fo/AC, (d) Spent Ru-Fo/AC, (e) Fresh Ru-Be/AC, (f) Spent Ru-Be/AC, (g) Fresh Ru-Foli/AC, (h) Spent Ru-Foli/AC. (About 100 particles were measured for all samples.)

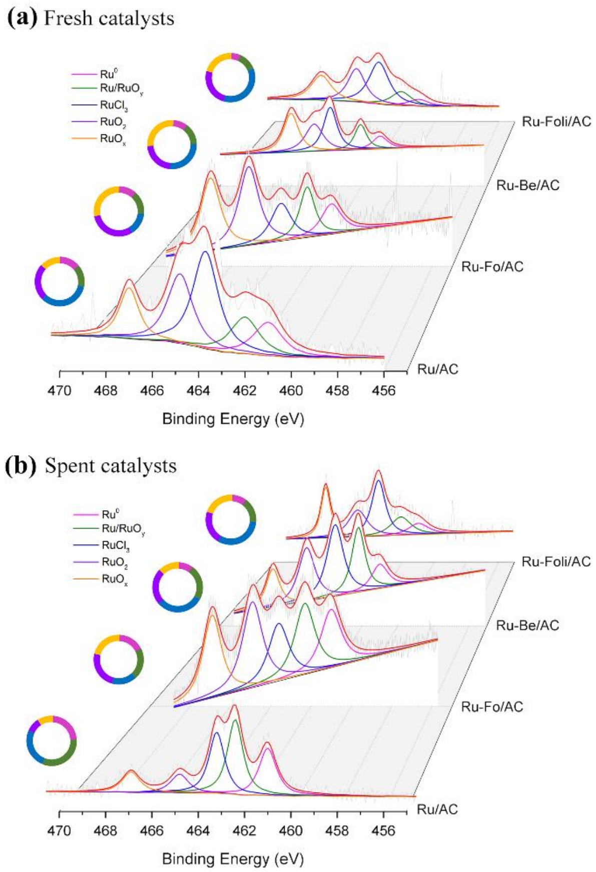


Fig. S7. XPS spectra of Ru 3p for fresh and spent Ru-based catalysts.

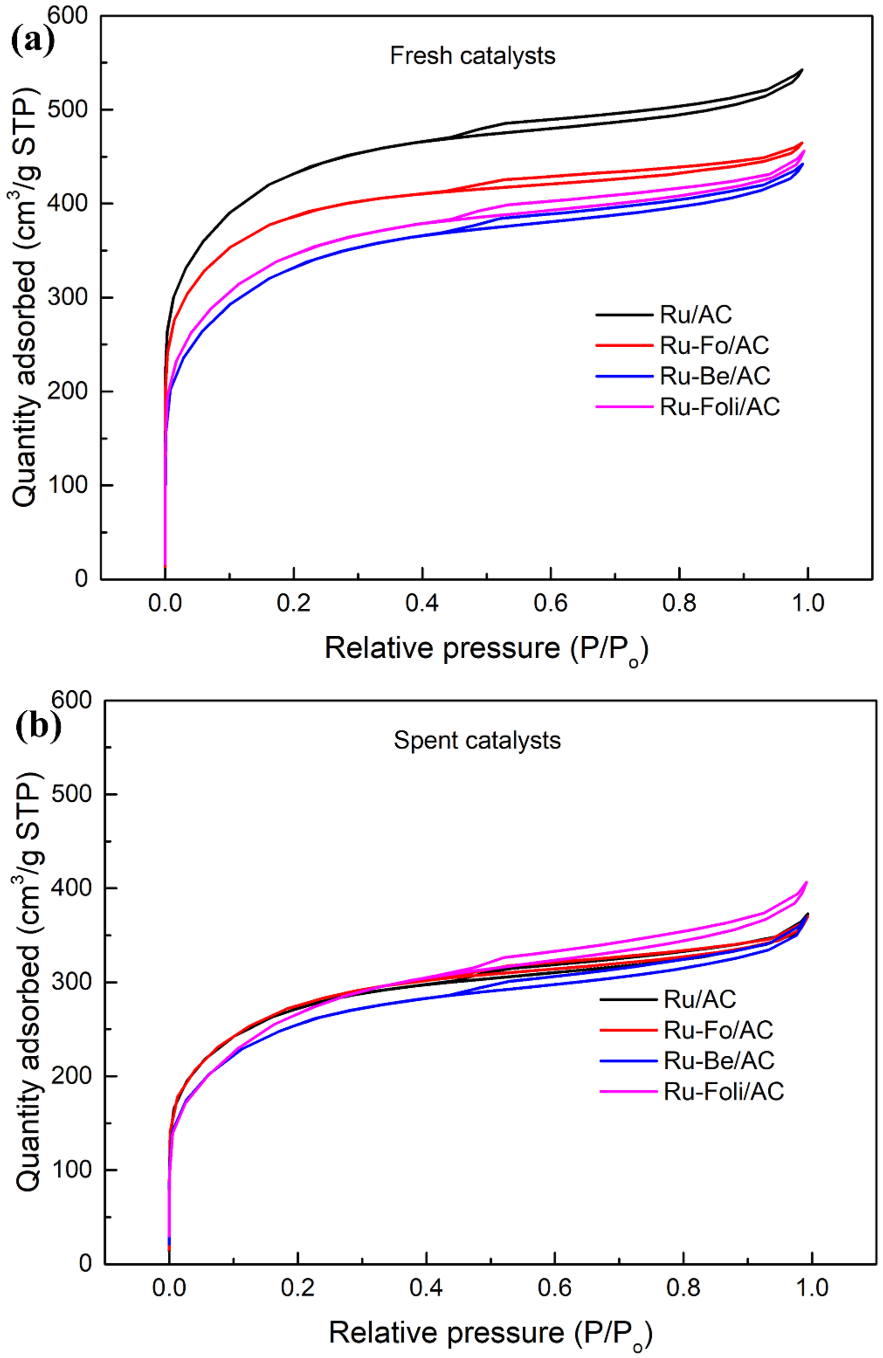


Fig. S8. N_2 adsorption-desorption isotherms of fresh and spent catalysts.

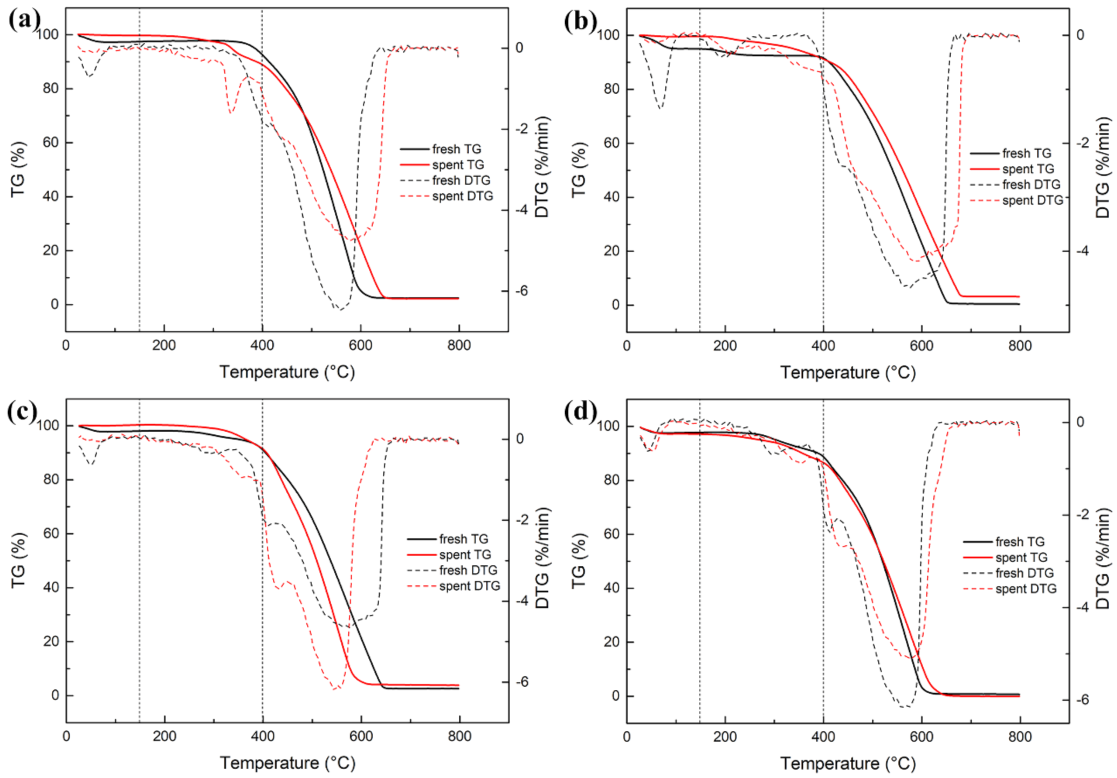
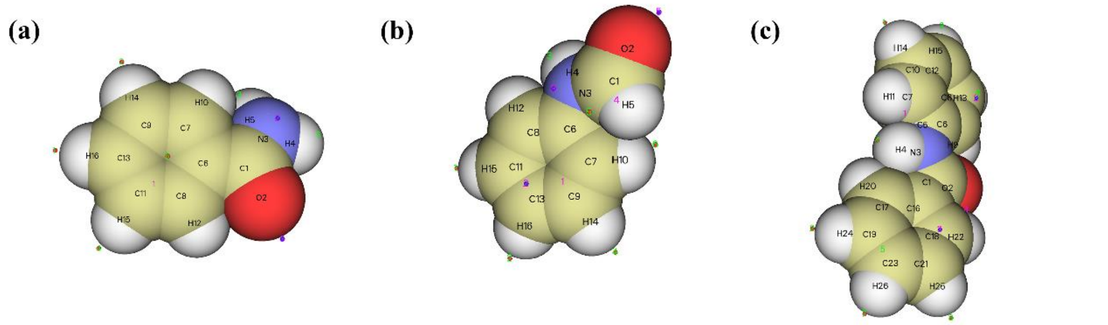


Fig. S9. TGA and DTG profiles of fresh and spent catalysts of (a) Ru/AC, (b) Ru-Fo/AC, (c) Ru-Be/AC and (d) Ru-Foli/AC.



(a)

Note: Average and variance below are in kcal/mol and (kcal/mol)^2 respectively

Atom#	All/Positive/Negative average			All/Positive/Negative variance		
1	-3.46238	2.87925	-5.56363	16.06478	2.99307	13.07171
2	-31.84807	NaN	-31.84807	NaN	NaN	73.73623
3	-6.21549	1.93186	-7.79663	10.63816	1.37335	9.26481
4	14.03769	19.62261	-7.21493	127.38149	101.38560	25.99589
5	23.83632	24.10697	-1.37887	129.33086	128.72191	0.60895
6	-7.26238	2.15833	-8.23445	19.20122	2.10267	17.09855
7	-5.59073	2.38017	-6.94088	13.32028	3.45037	9.86991
8	-10.31031	NaN	-10.31031	NaN	NaN	8.14199
9	-6.88852	0.23912	-6.91374	6.87749	0.00305	6.87444
10	11.71685	13.53573	-2.09551	54.78352	52.87400	1.90952
11	-8.87272	NaN	-8.87272	NaN	NaN	4.57304
12	-5.41461	3.56085	-9.58773	69.68014	3.93131	65.74883
13	-7.58159	NaN	-7.58159	NaN	NaN	5.51600
14	9.11065	10.19436	-1.66742	23.06811	21.77793	1.29017
15	5.71775	7.83749	-2.87968	17.17934	13.91745	3.26189
16	7.97911	9.33642	-1.91094	20.06451	18.67406	1.39045

ESP near phenyl is -17.38 kJ/mol

(b)

Note: Average and variance below are in kcal/mol and (kcal/mol)^2 respectively

Atom#	All/Positive/Negative average			All/Positive/Negative variance		
1	3.54363	5.53407	-2.36796	13.00894	10.96379	2.04516
2	-26.97933	NaN	-26.97933	NaN	NaN	88.36248
3	2.24988	3.07629	-0.55067	3.24624	3.15601	0.09023
4	18.20238	20.21557	-5.09149	146.24189	132.61138	13.63050
5	8.85297	10.98036	-6.55955	39.32832	19.20709	20.12123
6	-1.53664	2.15092	-3.70183	7.51462	2.77923	4.73539
7	-4.96091	0.98500	-5.23111	5.22168	0.47440	4.74728
8	-4.40367	2.20466	-4.93385	8.40978	3.36873	5.04104
9	-6.36618	NaN	-6.36618	NaN	NaN	3.99329
10	11.16561	11.92793	-1.37057	33.69731	32.78827	0.90905
11	-6.18901	NaN	-6.18901	NaN	NaN	4.24729
12	13.46726	13.94194	-1.04231	49.76984	49.25857	0.51127
13	-7.00117	NaN	-7.00117	NaN	NaN	3.42024
14	9.23992	10.24439	-1.37932	22.94233	22.18773	0.75460
15	9.59475	10.47612	-1.23972	24.24395	23.64395	0.60000
16	8.17948	9.61065	-1.90800	21.11765	19.74538	1.37227

ESP near phenyl is 21.19 kJ/mol

(c)

Note: Average and variance below are in kcal/mol and (kcal/mol)^2 respectively

Atom#	All/Positive/Negative average			All/Positive/Negative variance		
1	-0.17503	3.18679	-3.99317	9.85087	3.20273	6.64814
2	-27.68736	NaN	-27.68736	NaN	NaN	66.94053
3	-1.62722	2.15313	-3.25407	5.39715	2.19204	3.20511
4	22.88777	22.88777	NaN	NaN	154.26168	NaN
5	-8.39614	1.13029	-8.63741	12.76296	0.63124	12.13172
6	-14.16950	NaN	-14.16950	NaN	NaN	1.84489
7	-9.23234	1.04259	-9.35265	11.58850	0.47681	11.11169
8	-13.77619	NaN	-13.77619	NaN	NaN	3.29190
9	-10.80052	0.78190	-11.45467	48.26289	0.27281	47.99008
10	-11.35758	NaN	-11.35758	NaN	NaN	6.24860
11	12.03032	13.81159	-2.46886	60.01586	57.71822	2.29764
12	-12.86560	NaN	-12.86560	NaN	NaN	4.46315
13	1.15828	5.05107	-5.07669	16.33132	6.72486	9.60646
14	5.62655	8.17578	-3.44962	18.57037	14.22826	4.34211
15	3.04196	6.40125	-4.55530	16.29803	9.04877	7.24926
16	-4.94640	2.17681	-6.49069	15.25219	2.60071	12.65148
17	-3.29791	3.13054	-5.09575	10.65811	4.36758	6.29053
18	-8.10510	NaN	-8.10510	NaN	NaN	7.84832
19	-4.67435	1.08961	-4.90212	6.36206	0.77155	5.59051
20	15.23025	15.77347	-1.00795	63.32691	62.87253	0.45438
21	-6.74187	NaN	-6.74187	NaN	NaN	4.17625
22	-2.52851	4.75171	-8.09577	64.88762	7.27945	57.60817
23	-5.49001	0.12415	-5.50959	4.94016	0.00709	4.93307
24	11.13411	11.50590	-0.91661	27.64515	27.24797	0.39718
25	7.69101	9.05493	-1.92234	19.76773	18.12559	1.64214
26	9.81828	10.45891	-0.99376	23.95495	23.51495	0.43999

ESP near phenyl is -33.88 kJ/mol

Fig. S10. Electrostatic potential statistics on molecular surfaces near atoms of (a) benzamide, (b) formanilide, and (c) benzanilide.

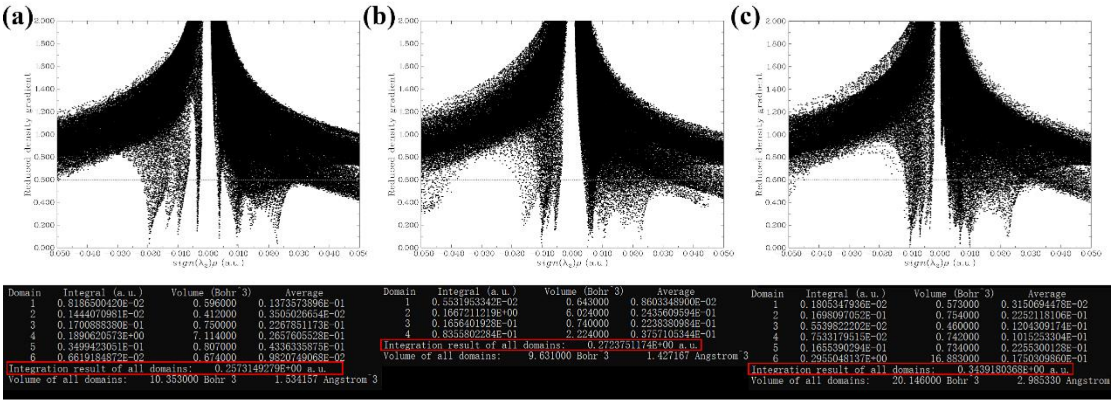


Fig. S11. Scatter graph of RDG function versus electron density multiplied and integration result of domains of (a) Ru-Be, (b) Ru-Foli, and (c) Ru-Beli.

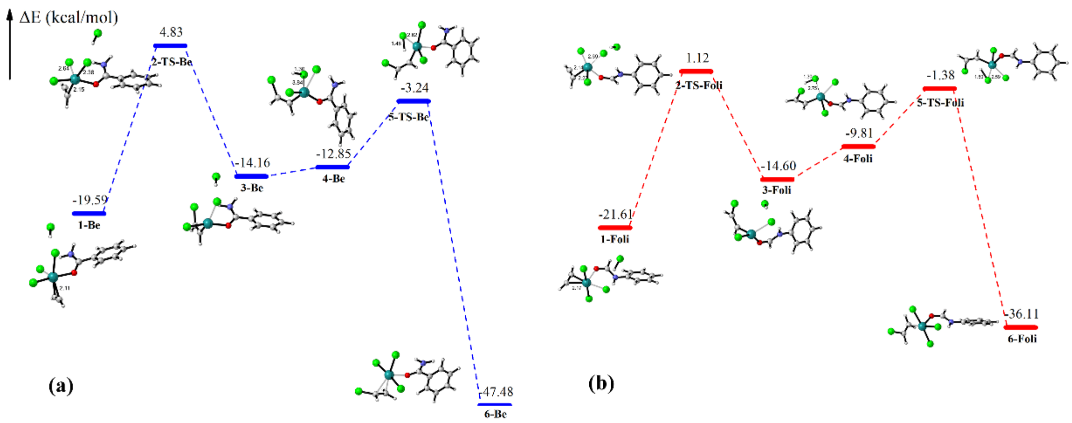


Fig. S12. Reaction paths of acetylene hydrochlorination over (a) Ru-Be/AC and (b) Ru-Foli/AC catalysts.

Table S2 Hirschfeld charge of $RuCl_3$ in Ru-Amide complexes

Ru-Amide complexes	Ru binding to O in amide ligands (e)	Ru binding to N in amide ligands (e)
Ru-Be	-0.25	-0.23
Ru-Foli	-0.26	-0.24
Ru-Beli	-0.30	-0.27

Table S3 Acetylene conversion over different Ru-based catalysts

Catalysts	Ru loading	Reaction condition	Acetylene conversion
Ru/AC-NHN[1]	1 wt%	180°C, 360h^{-1}	93.2%
Ru1-Co3/SAC[2]	1 wt%	170°C, 180h^{-1}	95.0%
Ru/SAC-N700[3]	1 wt%	170°C, 180h^{-1}	99.5%
Ru-in-CNT[4]	1 wt%	170°C, 90h^{-1}	99.1%
Ru/SAC-C300[5]	1 wt%	170°C, 180h^{-1}	96.5%
Ru1K1/SAC[6]	1 wt%	170°C, 180h^{-1}	93.4%
Ru1Co3Cu1/SAC[7]	0.1 wt%	170°C, 90h^{-1}	99.3%
Ru-10%DMPU/AC[8]	1 wt%	170°C, 900h^{-1}	87.6%
1%Ru@15%TPPB/AC[9]	1 wt%	170°C, 360h^{-1}	99.7%
Ru-L_1/AC[10]	1 wt%	180°C, 180h^{-1}	96.5%
Ru-L_8/AC[10]	1 wt%	180°C, 180h^{-1}	99.0%
IPr–(Ru)/AC[11]	1 wt%	180°C, 180h^{-1}	99.0%
Ru-Thi/AC[12]	1 wt%	170°C, 400h^{-1}	85.1%
0.5%Ru10%Foli/AC[This work]	0.5 wt%	160°C, 600h^{-1}	89.1%
0.5%Ru10%Beli/AC[This work]	0.5 wt%	160°C, 600h^{-1}	92.1%
0.2%Ru10%Beli/AC[This work]	0.2 wt%	160°C, 240h^{-1}	95.1%

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