Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Exceptionally Stable Rh-based Molecular Catalyst Heterogenized on a Cationically charged Covalent Triazine Framework Support for Efficient Methanol Carbonylation

Kwangho Park[a], Sangyup Lim[a], Joon Hyun Baik[b], Honggon Kim[c], Kwang-Deog Jung[c], and Sungho Yoon*[a]

[a] Department of Bio & Nano Chemistry Kookmin University 861-1 Jeongneung-dong, Seongbuk-gu, Republic of Korea

[b]Climate and Energy Research group, Research Institute of Industrial Science & Technology (RIST), 67 Cheongam-ro, Pohang 37673, Republic of Korea.

[c]Clean Energy Research Centre, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 136-791, Republic of Korea

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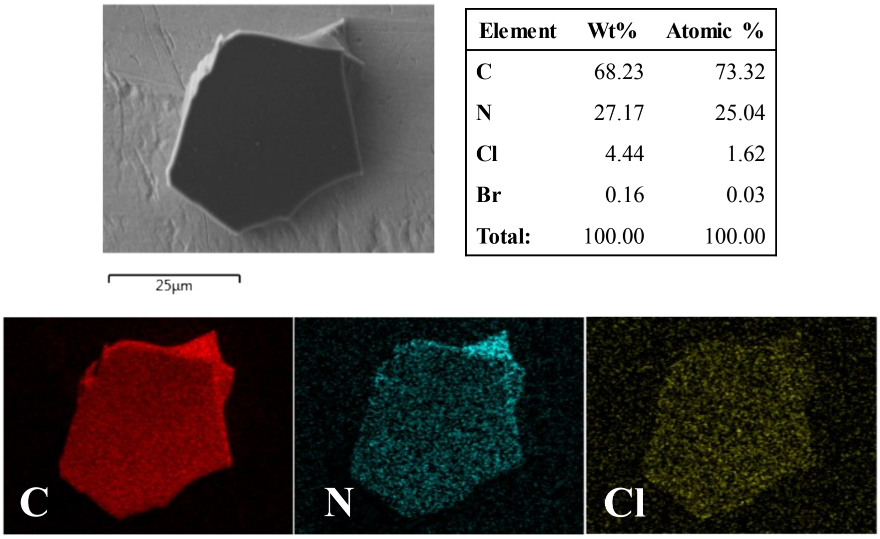
1. Characterization of bpim-CTF support



Element	Wt%	Atomic %
C	68.23	73.32
N	27.17	25.04
Cl	4.44	1.62
Br	0.16	0.03
Total:	100.00	100.00

Fig S1. SEM & EDS for bpim-CTF support

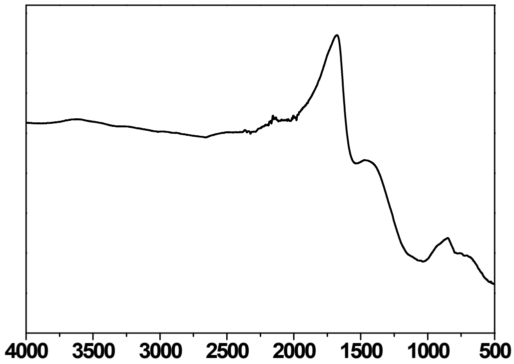


Fig S2. FT-IR Measurement of bpim-CTF support

* The spectra was obtained by ATR technique

Element	Wt%
C	48.42
N	14.51
H	4.52
C/N	3.34

Table S1. Elemental analysis of bpim-CTF support

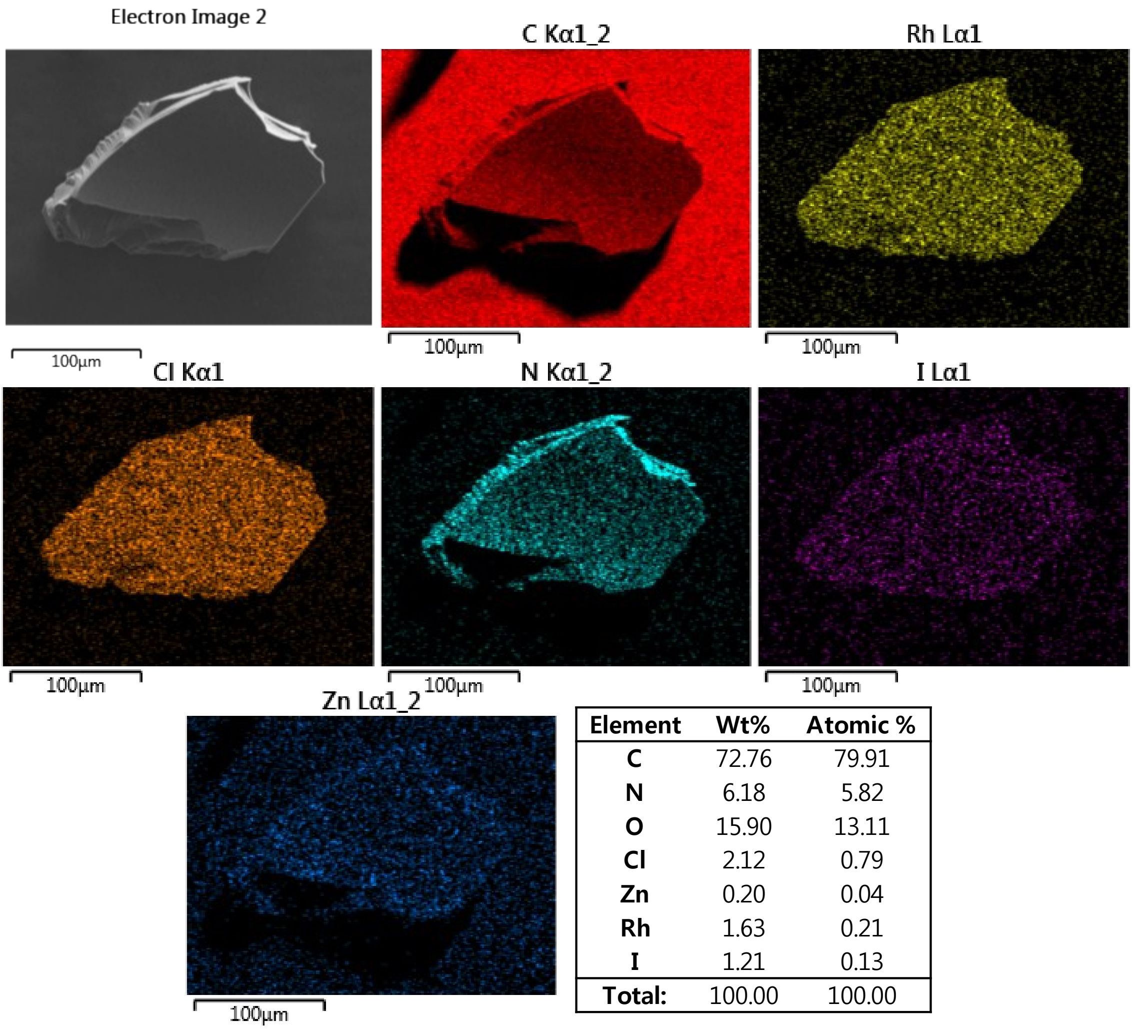
2. Screening catalytic activity according to the catalyst porosity

Entry	$a_{s,BET}$	$V_{pore,\ tot}$	V_{mean}	Conv.[a]	Select.	
	[$m^2\ g^{-1}$]	[$cm^3\ g^{-1}$]	[nm]	MeOH [%]	MA [%]	AA [%]
Rh-bpim-CTF-400	732	0.31	1.70	31.7	91.1	8.9
Rh-bpim-CTF-500	1650	0.79	1.91	93.0	44.0	56.0

Reaction conditions: 0.2 g of Rh-bpim-CTFs, $W/F_m = 7.6$, Temperature = 240°C, and Pressure = 10 bar.

Table S2. Pore parameters of bpim-CTF support synthesized at different temperatures, and catalytic activity evaluation.

3. SEM and EDS measurements for Rh-bpim-CTF



Element	Wt%	Atomic %
C	72.76	79.91
N	6.18	5.82
O	15.90	13.11
Cl	2.12	0.79
Zn	0.20	0.04
Rh	1.63	0.21
I	1.21	0.13
Total:	100.00	100.00

Figure S3. SEM & EDS mapping of Rh-bpim-CTF

4. Nitrogen physisorption measurements.

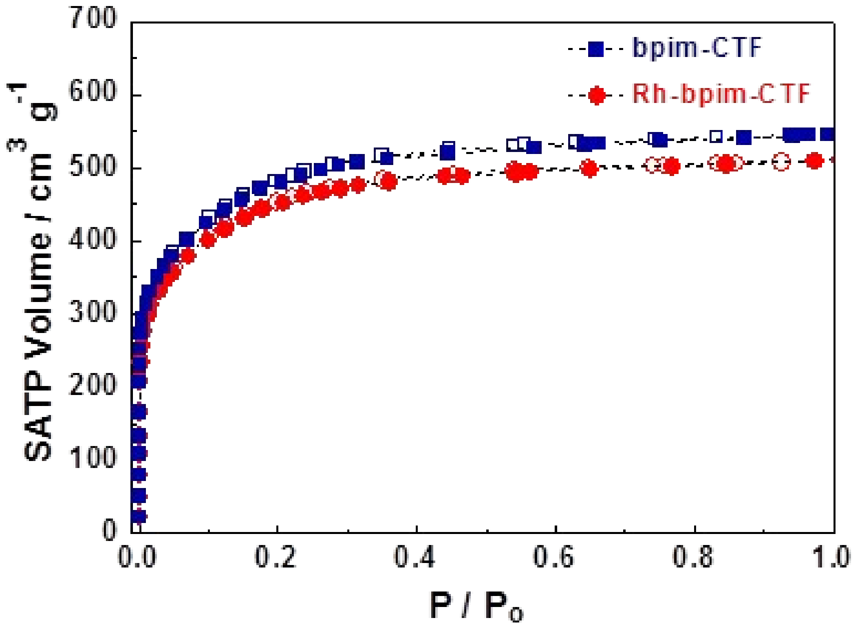


Figure S4. Nitrogen sorption isotherms of bpim-CTF support and Rh-bpim-CTF at 77 K

5. XPS analysis

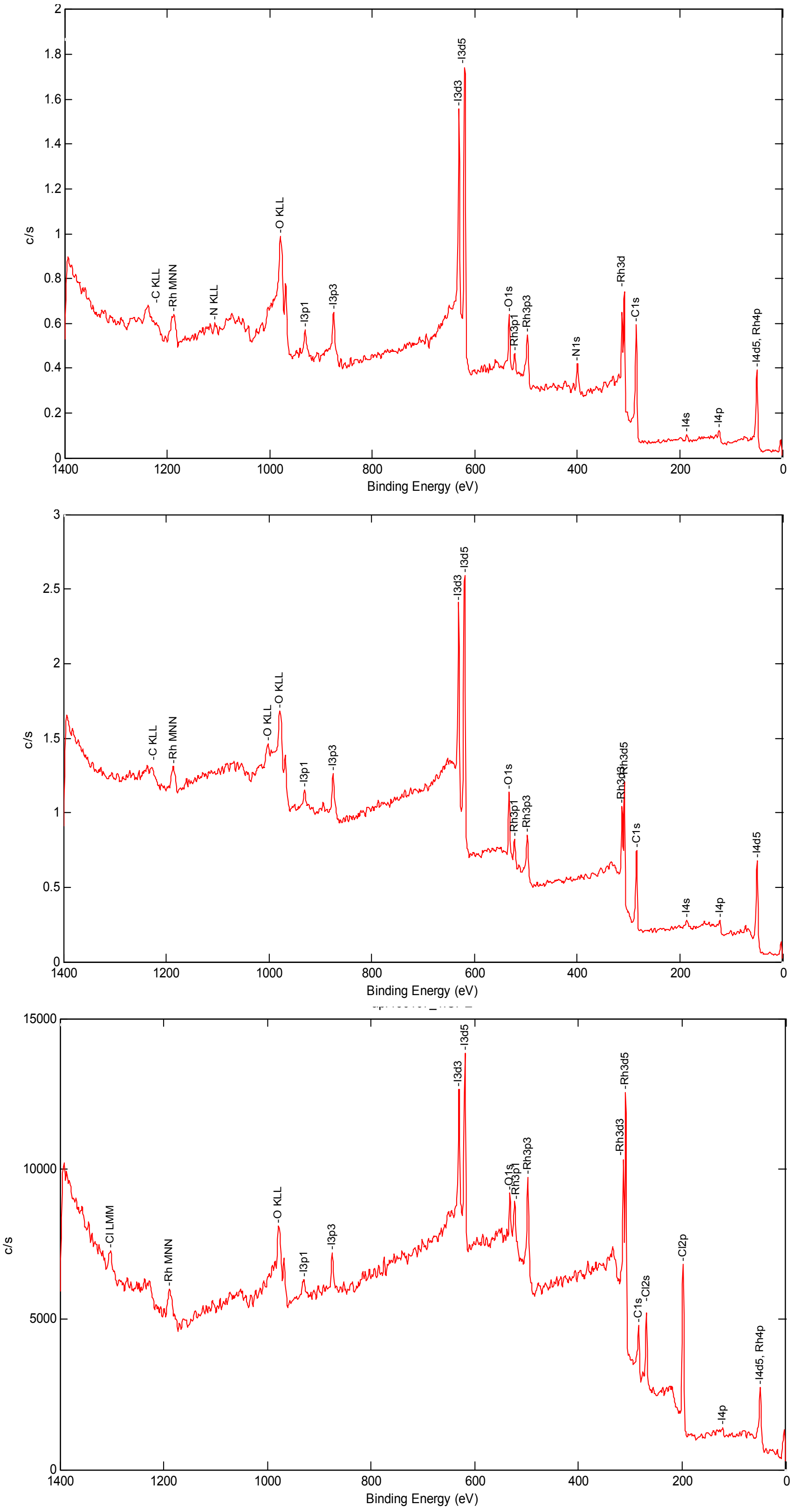


Figure S5. XPS of Rh-bpim-CTF (top), $[Rh(CO)_2I]_2$ (middle), and $RhCl_3$ xH_2O(bottom).

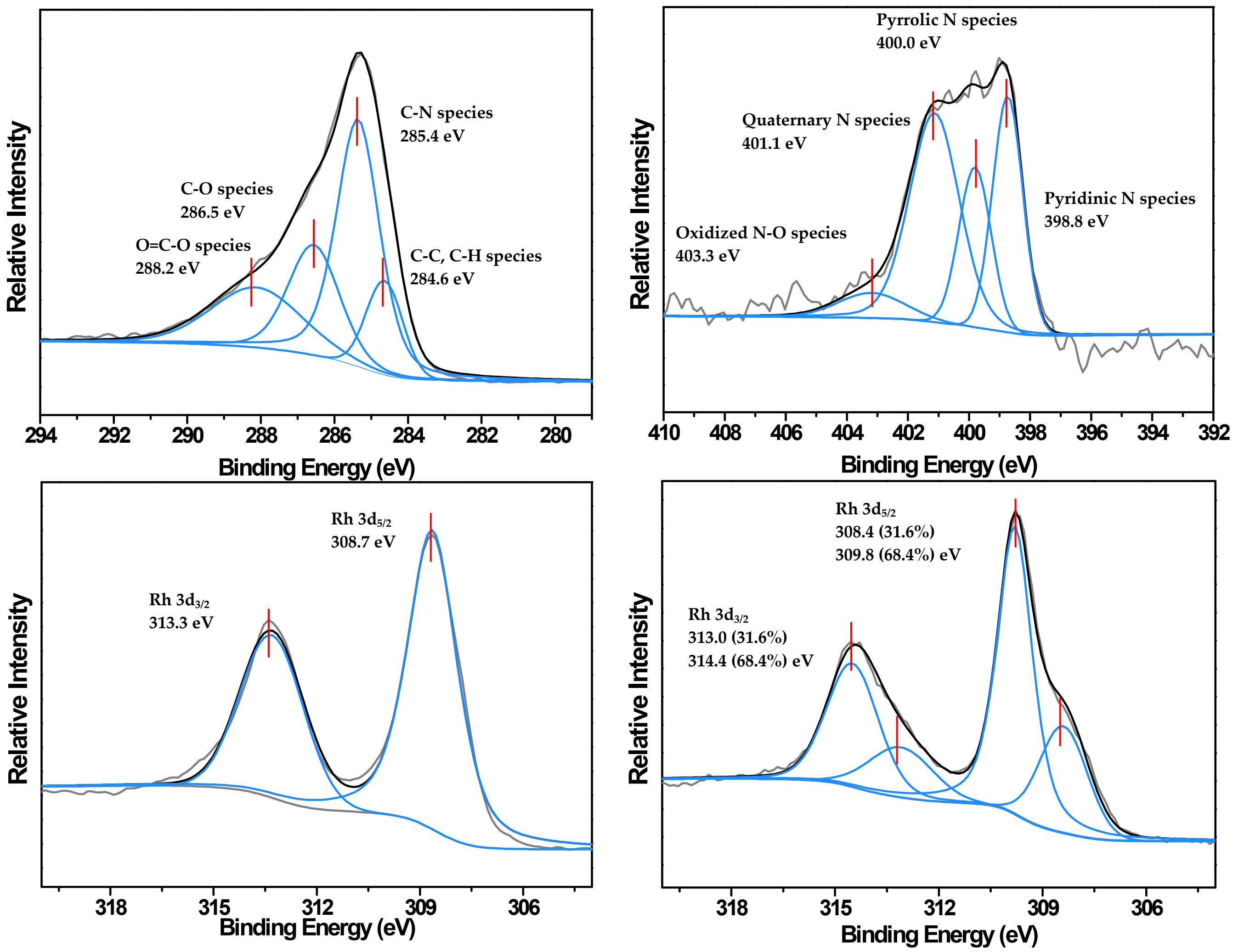


Figure S6. Deconvoluted C 1s (top left), N 1s (top right) spectrum of Rh-bpim-CTF and Rh 3d5 spectrum of $[Rh(CO)_2I]_2$ (bottom left) and $RhCl_3$ xH_2O.

	C1s[a]	N1s[a]	O1s[a]	Rh3d5[a]	I3d5[a]
Rh-bpim-CTF	64.6	10.0	12.1	6.3	8.0
$[Rh(CO)_2I]_2$	89.9	0	6.2	1.9	2.0

Table S3. Atomic composition of Rh-bpim-CTF and $[Rh(CO)_2I]_2$ by XPS

[a] Atomic %;

6. FT-IR measurements.

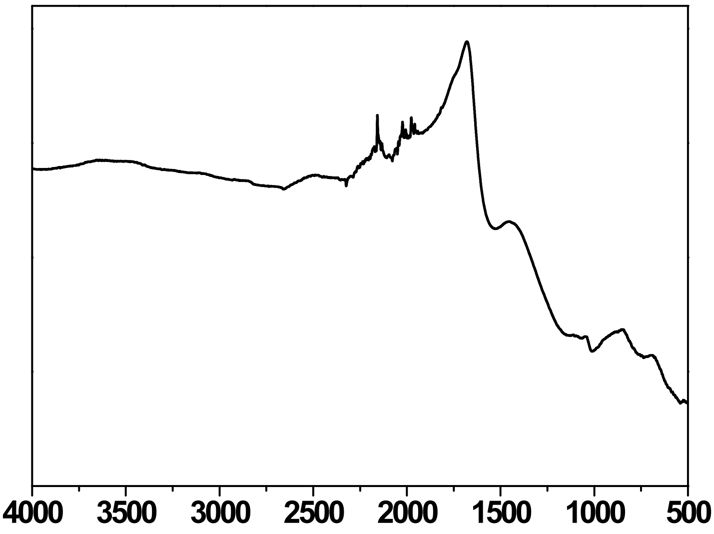


Figure S7. FT-IR spectrum of Rh-bpim-CTF

* The spectra was obtained by ATR technique

7. Methanol carbonylation process.

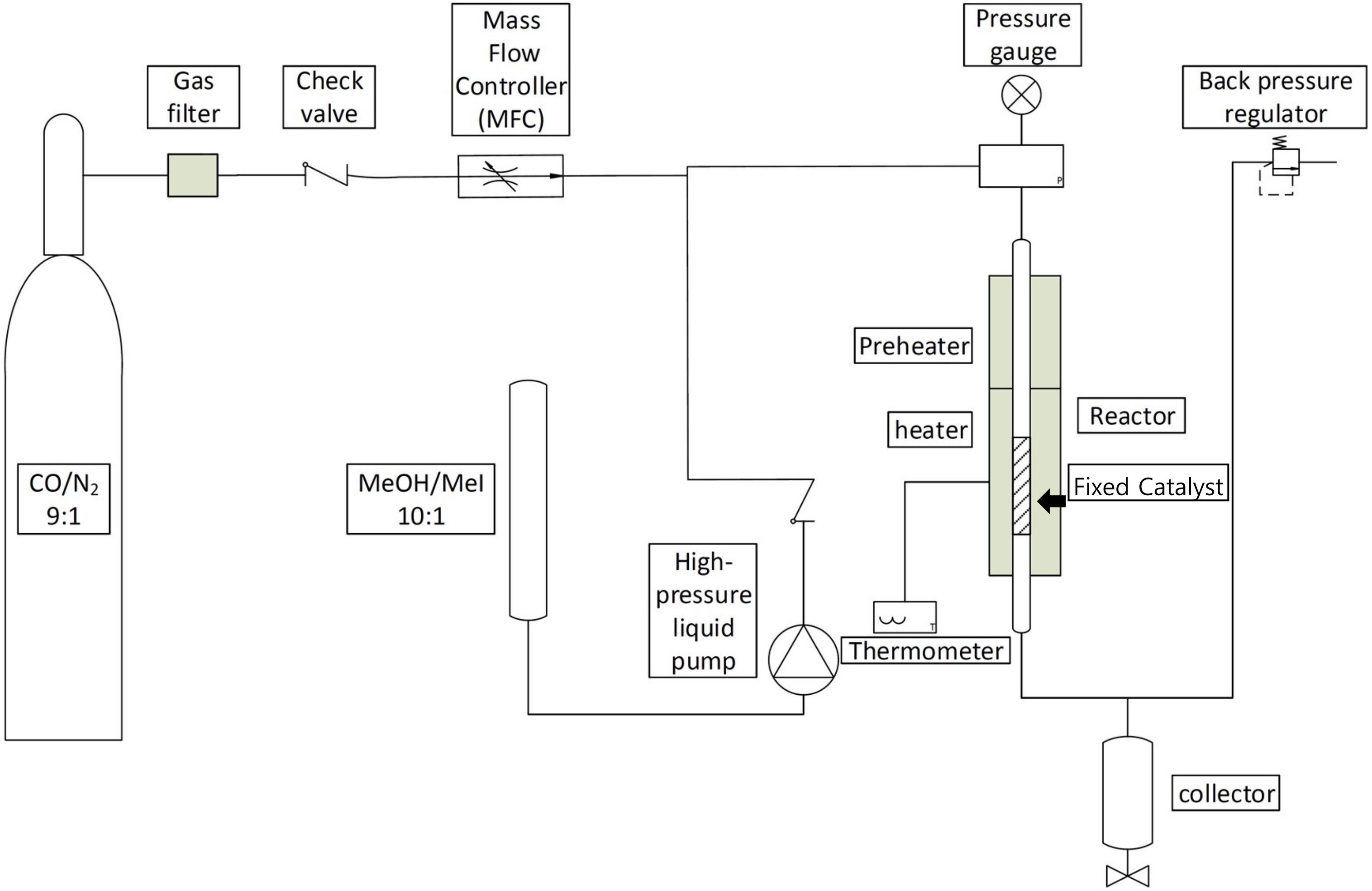


Figure S8. Schematic diagram of gas-phase methanol carbonylation using Rh-bpim-CTF

8. Feed flow reagents conditions

Table S4. Feed flow reagents conditions

CO[a]	N_2[a]	MeOH[b]	MeI[b]	F_m[c]	W/F_m[d]
[ml min^{-1}]		[ml h^{-1}]		[mol h^{-1}]	[g h mol^{-1}]
52.0	6.00	4.24	0.64	0.104	1.9
39.0	4.50	3.18	0.48	0.078	2.5
26.0	3.00	2.12	0.32	0.052	3.8
13.0	1.50	1.06	0.16	0.026	7.6

[a]Volume of gas phase feed reagents per hour [b]Volume of liquid-phase feed reagents per hour [c]Mole quantity of methanol feed flow per hour [d]W/F_m = 0.2 g (amount of catalyst) / desired F_m

9. Catalytic activity evaluation in various conditions.

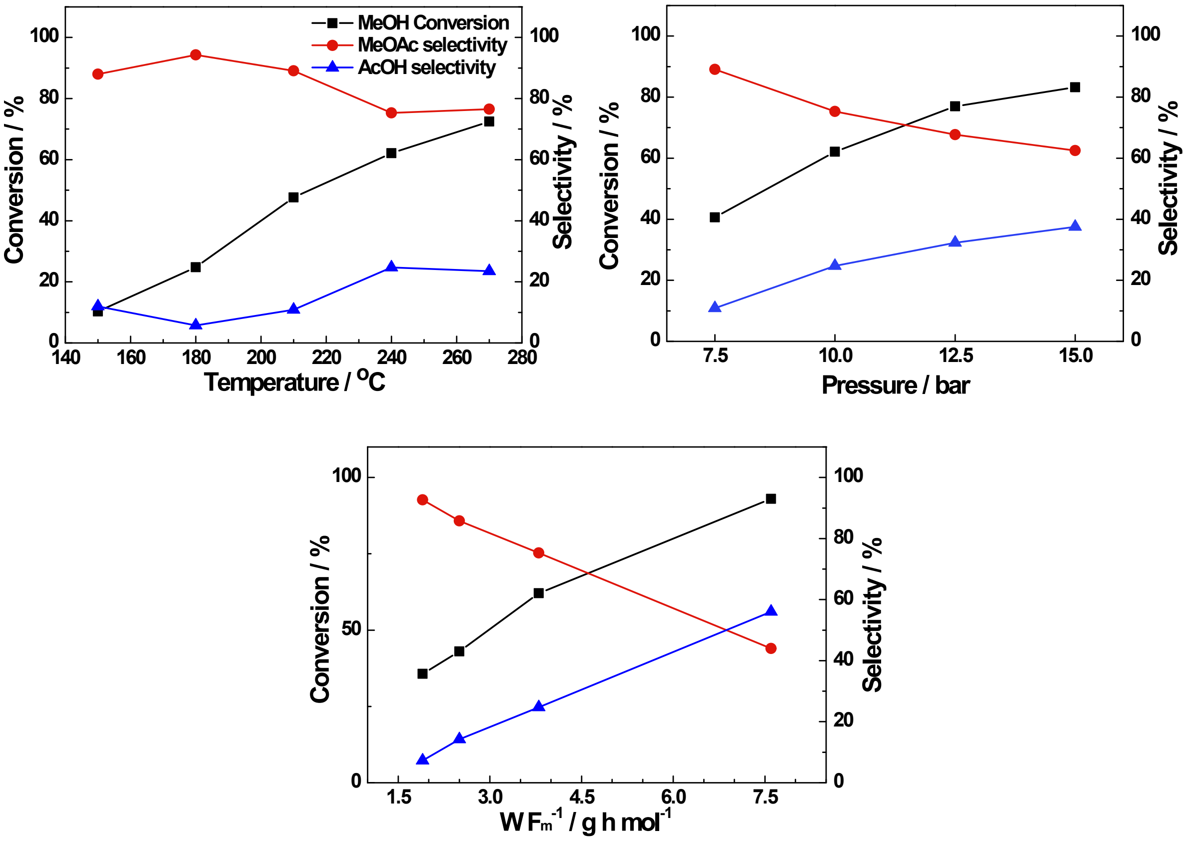


Figure S9. Methanol conversion, methyl acetate and acetic acid selectivities over the Rh-bpim-CTF according to the effect of the temperature (top left), pressure (top right), contact time of feed flow (bottom center) carbonylation

10. Catalytic activity evaluation with Rh-doped non-charged CTF catalyst

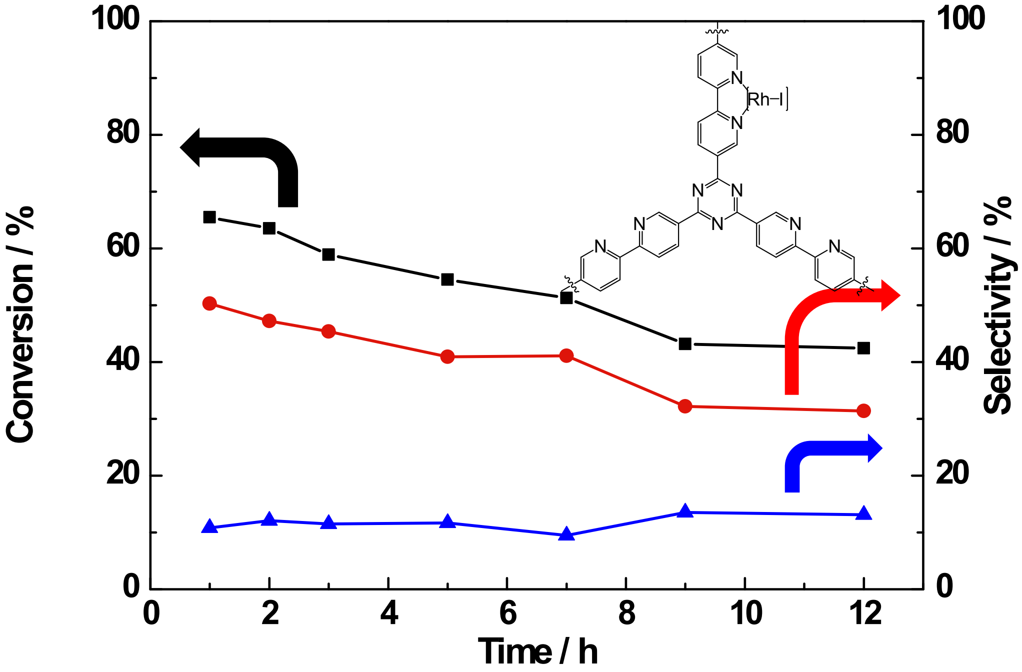


Figure S10. Methanol conversion(black), methyl acetate(red) and acetic acid(blud) selectivities over the Rh-bpy-CTF with continuous flow methanol carbonylation
* Reaction conditions: 0.2 g of Rh-bpim-CTFs, $W/F_m = 7.6$, Temperature = 240°C, and Pressure = 10 bar.

11. Thermal stability analysis

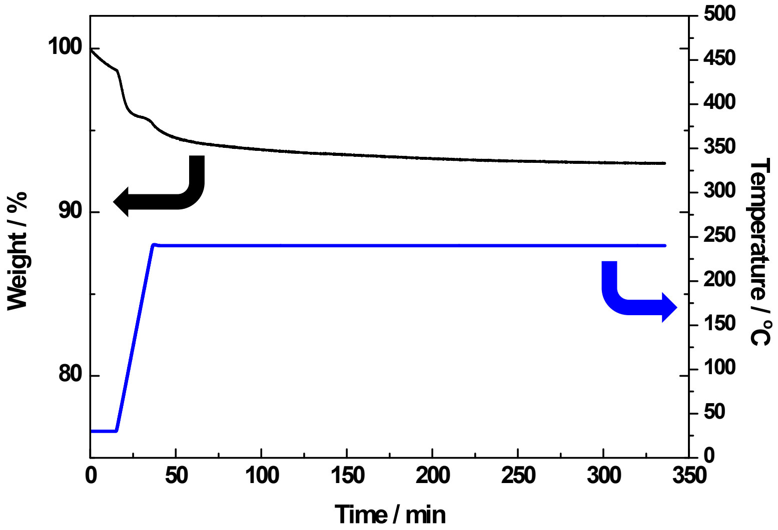


Figure S11. Isothermal TGA measurement of Rh- bpim-CTF at 240 °C

12. **TEM analysis**

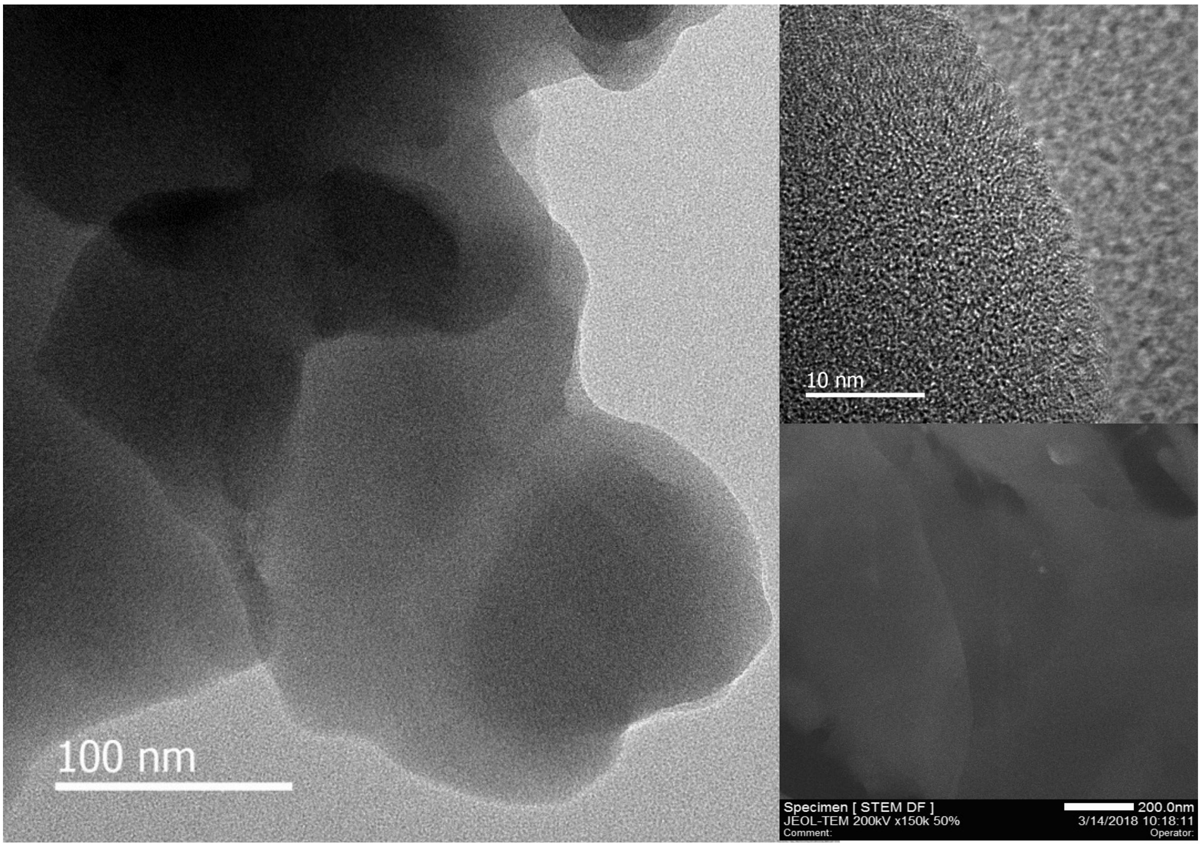


Figure S12. HR-TEM image with low magnification (left), high magnification (top right), and HADDF-TEM image (bottom right) of Rh-bpim-CTF after continuous methanol carbonylation