Supplementary information

Synthesis of ethanol via methanol homologation with CO_2 and H_2 using an industrially relevant Ru-Co catalyst

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Table S1 Prices of Medications Used in the Experiment.

Entry	Catalyst precursor	Brand	Price (yuan per gram)
1	$RuCl_3$	Innochem	133
2	$CoCl_2$	Acros	128
3	$RuCl_3 \cdot 3H_2O$	Innochem	85
4	$CoCl_2 \cdot 6H_2O$	Innochem	7
5	$[Ru(CO)_3Cl_2]_2$	Apinno	1629
6	$Co_4(CO)_{12}$	Alfa	612
7	$RuBr_3$	Macklin	2700
8	RuI_3	Alfa	1369
9	$CoBr_2$	Alfa	17.8
10	CoI_2	Innochem	33
11	$Ru_3(CO)_{12}$	Innochem	277

Note: The above price information was collected from https://www.inno-chem.com.cn/ in August 2024.

Table S2 The amounts of other byproducts formed in Table 1.

Entry	Ru/Co (μmol)	Methanol substrate (mmol)	Ethanol selectivity (%)	Ethanol produced (mmol)	CO produced (mmol)	CH_4 produced (mmol)
1	5/240	6.3	62.4	1.43	0.67	0.86
2	5/240	12.5	61.8	2.10	0.71	1.30
3	10/240	12.5	58.5	2.27	0.61	1.61
4	10/360	12.5	64.9	2.58	0.30	1.40
5	10/480	12.5	55.4	2.47	0.50	1.99
6	15/720	18.8	37.6	1.50	0.44	2.49

Reaction conditions: a certain amount of $RuCl_3 \cdot 3H_2O$ and $CoCl_2 \cdot 6H_2O$, 3 mmol LiI, 2 mL NEP, (activation condition: 6 MPa CO, 200 °C, 12 h), a certain amount of methanol, 2 MPa CO_2 and 6 MPa H_2, 170 °C, 15 h of reaction.

Table S3 The amounts of other byproducts formed in Table 2.

Entry	Catalyst precursors	Methanol substrate (mmol)	Ethanol selectivity (%)	Ethanol produced (mmol)	CO produced (mmol)	CH_4 produced (mmol)
1*	Ru/LiI	0	-	0	1.35	0
2	Co/LiI	12.5	12.8	0.14	0	0.98
3	Ru/Co/LiI	12.5	47.8	1.64	0	1.79
4	Ru/Co/LiI	12.5	64.9	2.58	0.30	1.40
5	Ru/Co	12.5	-	0	0.60	0.12
6*	Ru/Co/LiI	0	-	0	1.11	0

Reaction conditions: 10 μmol $RuCl_3 \cdot 3H_2O$ and/or 360 μmol $CoCl_2 \cdot 6H_2O$, and/or 3 mmol LiI, 2 mL NEP, (activation condition: 6 MPa CO, 200 °C, 12 h), after catalyst activation the reaction was conducted at the following conditions: 12.5 mmol methanol if used, 2 MPa CO_2 or 0.5 MPa CO, and 6 MPa H_2, 170 °C, 15 h of reaction. * CO was detected, while no methane was observed after the reaction.

Table S4 Effect of different dosages of $RuCl_3 \cdot 3H_2O/CoCl_2 \cdot 6H_2O$ on ethanol synthesis from methanol, CO_2 and H_2.

Entry	Ru/Co (μmol)	Methanol conversion (%)	Ethanol Selectivity (%)	STY of ethanol ($g \cdot L^{-1} \cdot h^{-1}$)
1	5/240	42.4	48.8	2.0
2	10/240	58.5	38.6	1.9
3	20/240	63.5	34.8	1.1
4	30/240	76.9	21.5	1.1
5	40/240	76.5	20.0	1.1
6	50/240	85.4	13.2	1.1
7	40/180	84.4	13.5	1.0
8	40/300	78.1	21.6	1.6
9	40/450	77.2	25.8	1.9
10	40/600	78.3	25.1	1.9

Reaction conditions: a certain amount of $RuCl_3 \cdot 3H_2O$ and $CoCl_2 \cdot 6H_2O$, 3 mmol LiI, 2 mL NEP, (activation condition: 6 MPa CO, 200 °C, 12 h), 12.5 mmol methanol, 2 MPa CO_2 and 6 MPa H_2, 170 °C, 15 h of reaction.

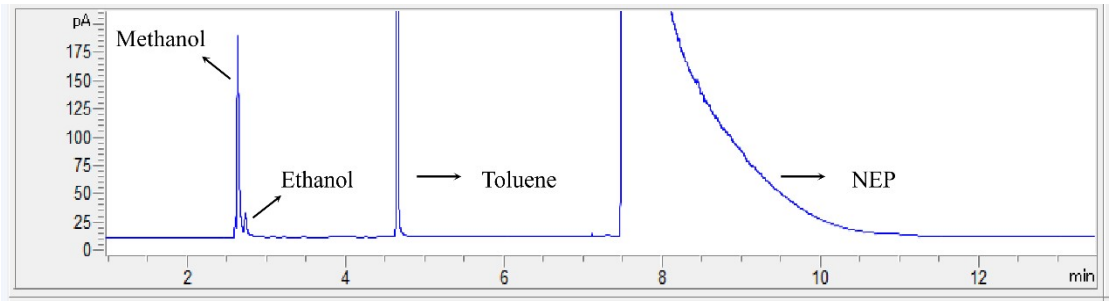

Fig. S1 GC spectrum of reaction solution obtained without CO activation of the Ru/Co precursors.

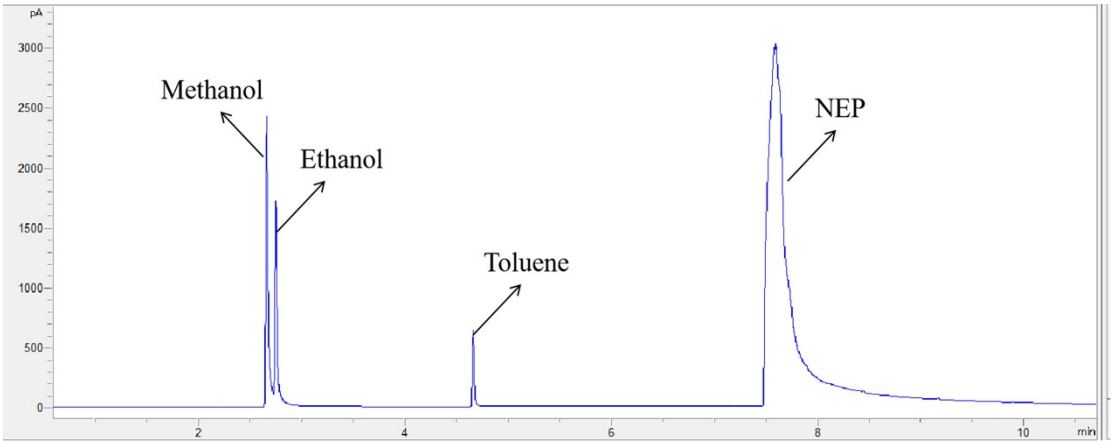

Fig. S2 GC spectrum of reaction solution obtained under optimal conditions.

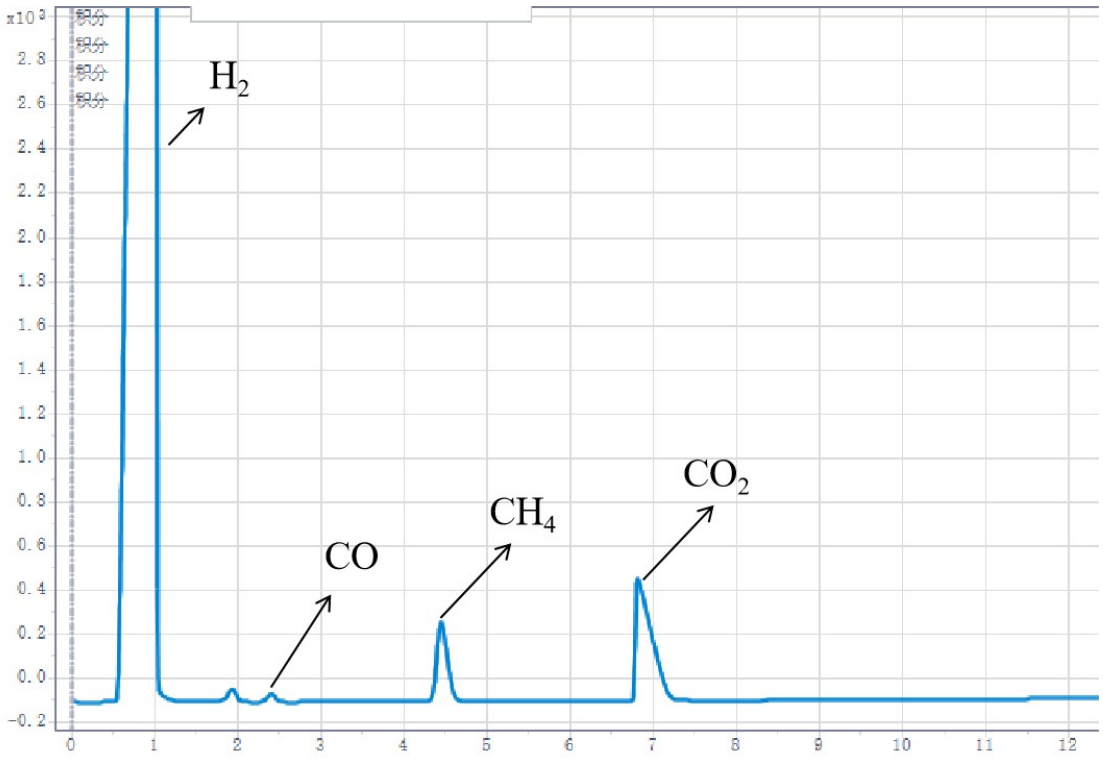

Fig. S3 GC spectrum of gas products after the reaction under optimal conditions.

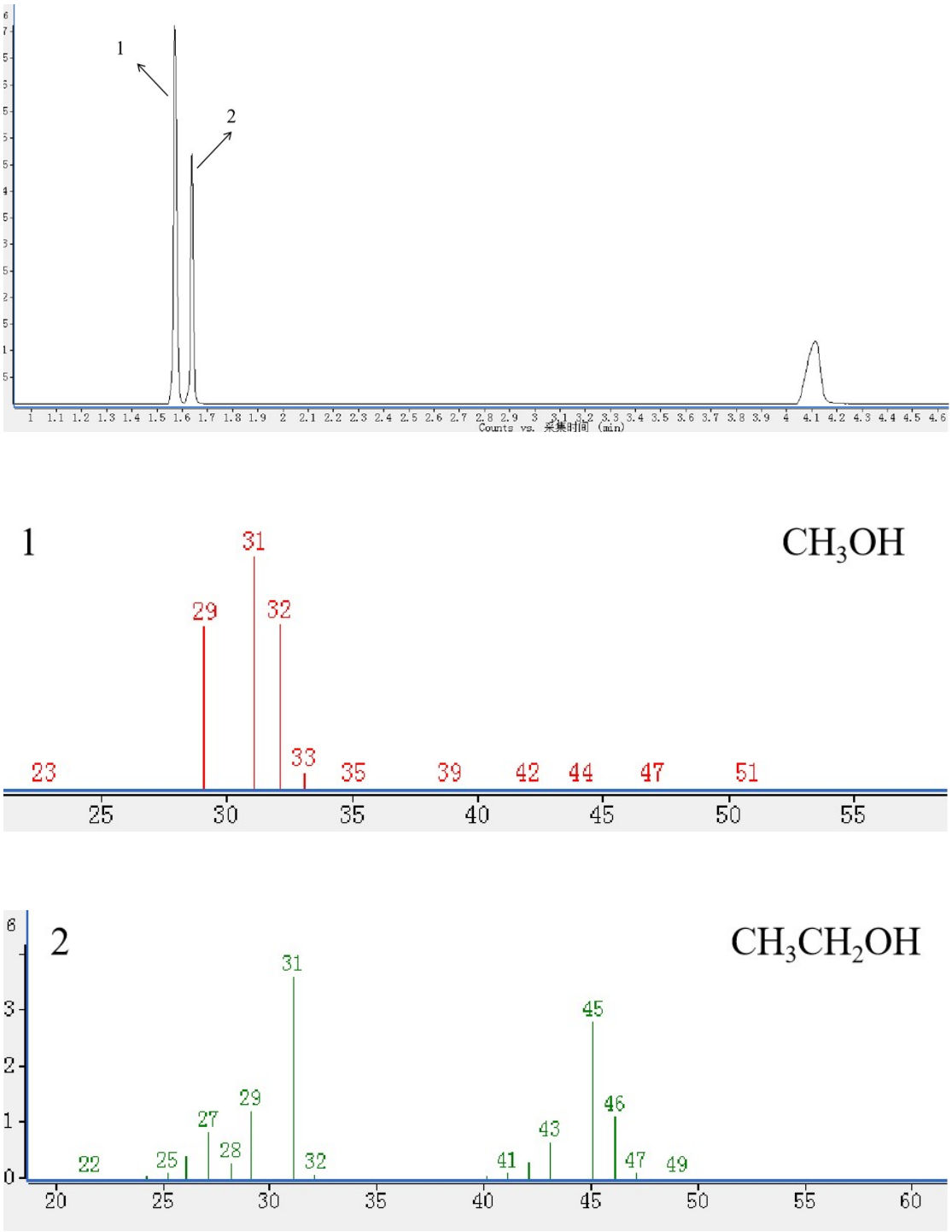

Fig. S4 GC-MS spectra of the reaction solution obtained at the optimized condition.

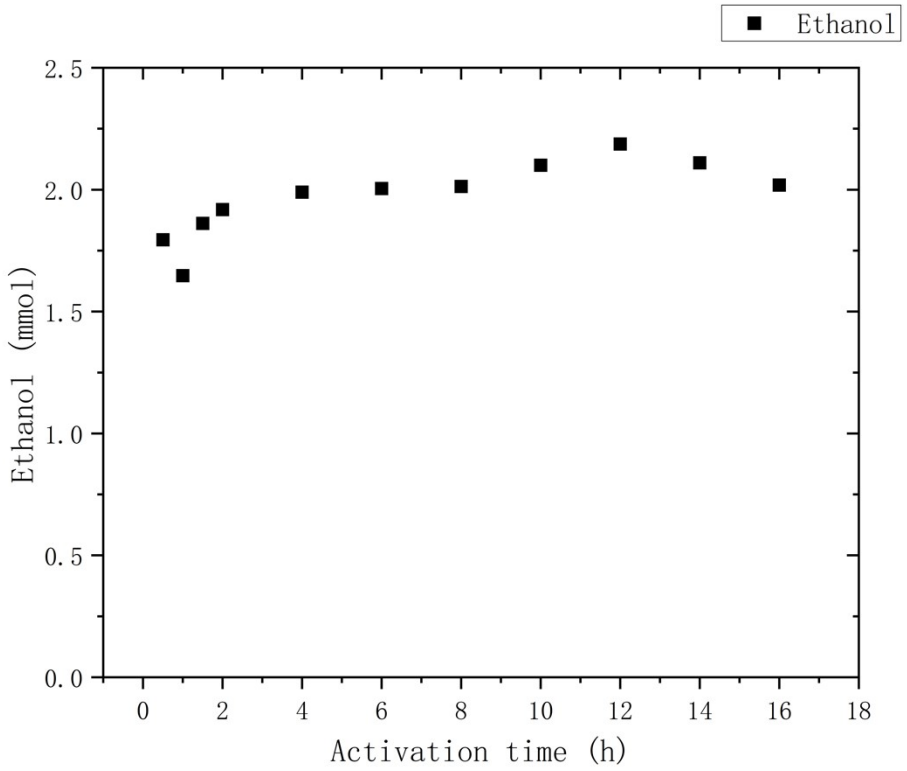

Fig. S5 The reaction results using the catalyst precursors activated for different time.

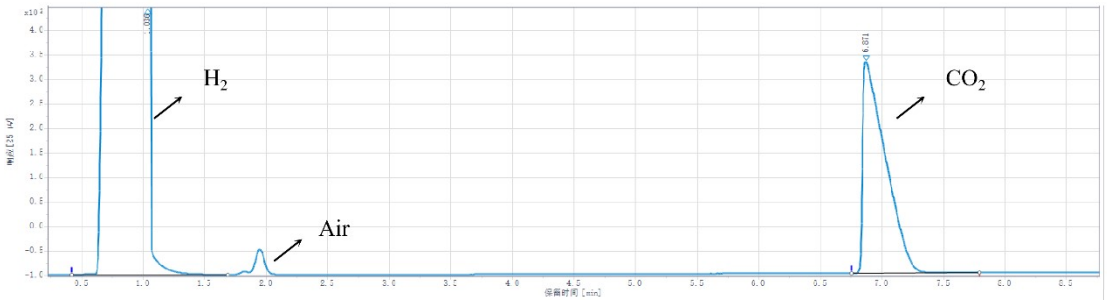

Fig. S6 GC spectrum of gas products after the reaction of CO_2 and H_2 catalyzed by the Co catalyst and LiI promoter.

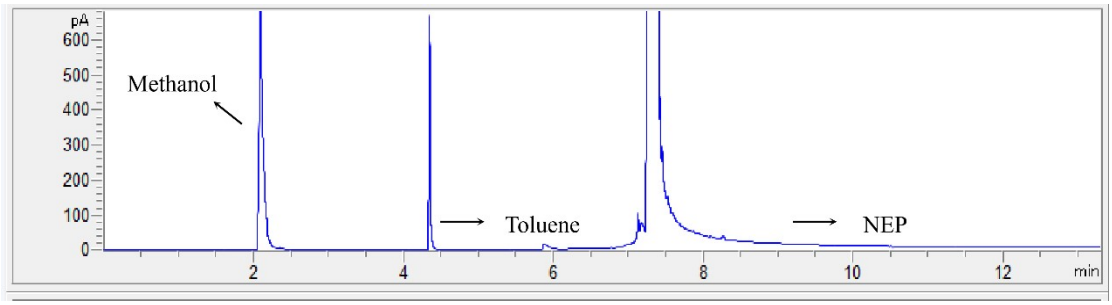

Fig. S7 GC spectrum of the solution after the reaction of methanol, CO_2 and H_2 catalyzed by the Co catalyst and LiI promoter.

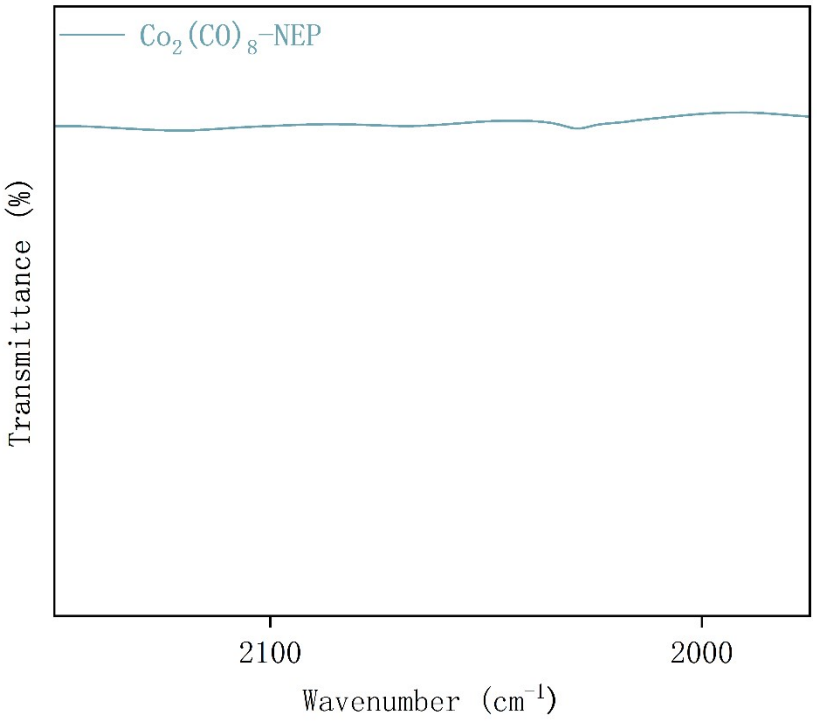

Fig. S8 FTIR image of $Co_2(CO)_8$-NEP standard solution.

Fig. S9 The batch reactors with a capacity of 25 mL.

Fig. S10 The batch reactor with a capacity of 3 L.