Electronic Supplementary Information

Synthesis of ethanol from paraformaldehyde, CO\textsubscript{2} and H\textsubscript{2}

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Figures

Fig. S1 The representative GC spectra of (a) liquid sample with internal standard toluene and (b) gaseous sample after the reaction of (CH$_2$O)$_n$ with CO$_2$ and H$_2$. Reaction conditions were the same as that of entry 1 in Table 1.
Target 1
The GC-MS spectra of the liquid product after the reaction of \((\text{CH}_2\text{O})_n\) with \(\text{CO}_2\) and \(\text{H}_2\). Reaction conditions were the same as that of entry 1 in Table 1.

**Fig. S2** The GC-MS spectra of the liquid product after the reaction of \((\text{CH}_2\text{O})_n\) with \(\text{CO}_2\) and \(\text{H}_2\). Reaction conditions were the same as that of entry 1 in Table 1.
Target 1
Target 2

CH₂OH

1³CH₂CH₂O⁻
**Fig. S3** The GC-MS spectra of reaction solution using \(^{13}\text{CH}_2\text{O})_n\) instead of \((\text{CH}_2\text{O})_n\). Other reaction conditions were the same as that of entry 1 in Table 1.

Notes:
1. The molecular weight of ethanol formed in the reaction was 47 Daltons. This demonstrates that the two C atoms in the ethanol product were from C of \((\text{CH}_2\text{O})_n\) and C of CO\(_2\), respectively.
2. According to fragment analysis, the C atom of CH\(_3\) group in ethanol product was from \((\text{CH}_2\text{O})_n\).
Fig. S4 The $^1$H NMR (a) and $^{13}$C NMR (b) spectra of reaction solution using (CH$_2$O)$_n$, and the $^1$H NMR (c) and $^{13}$C NMR (d) spectra of reaction solution using (CH$_2$O)$_n$. Reaction conditions were the same as that of entry 1 in Table 1.

Notes: From the $^1$H NMR spectra (c) of the $^{13}$C-labelled reaction, it can be seen that the proton signal of CH$_3$ group on the ethanol product splits into three peaks compared to the standard spectra (a), which is caused by the coupling with $^{13}$C atom. From the $^{13}$C NMR spectra (d) of the $^{13}$C-labelled reaction, it can be observed that the C signal of CH$_3$ group was abnormally high in contrast to the standard spectra (b). In addition, the C signal of CH$_2$ group splits into triple peaks, which is caused by the coupling with the adjacent $^{13}$C atom in the CH$_3$ group. Both $^1$H NMR and $^{13}$C NMR spectra confirmed that the C atoms of CH$_3$ group in ethanol product are mostly from (CH$_2$O)$_n$. 
Target 1
Target 2
**Fig. S5** The GC-MS spectra of reaction solution using (CD$_2$O)$_n$ instead of (CH$_2$O)$_n$. Other reaction conditions were the same as that of entry 1 in Table 1.
Target 2
Fig. S6 The GC-MS spectra of reaction solution using D₂ instead of H₂. Other reaction conditions were the same as that of entry 1 in Table 1.
The GC spectra of reaction solution after hydrogenation of (CH$_2$O)$_n$ by Ru catalyst. Reaction conditions: 7.5 μmol Ru(acac)$_3$, 3 mmol LiI, 2 mL DMI, 3.2 mmol “CH$_2$O” monomer (0.1 g), 5 MPa H$_2$ (at room temperature), 180 °C, 1 h.
Fig. S8 The GC spectra of reaction solution after hydrogenation of \((\text{CH}_2\text{O})_n\) by Co catalyst. Reaction conditions: 45 \(\mu\text{mol}\) CoBr$_2$, 3 mmol LiI, 2 mL DMI, 3.2 mmol “\text{CH}_2\text{O}” monomer (0.1 g), 5 MPa H$_2$ (at room temperature), 180 °C, 1h.
**Fig. S9** The GC spectra of (a) liquid sample and (b) gaseous sample after the CO\(_2\) hydrogenation catalyzed by Ru(acac)$_3$ catalyst. Reaction conditions: 7.5 μmol Ru(acac)$_3$, 3 mmol LiI, 2 mL DMI, 3 MPa CO\(_2\) and 5 MPa H\(_2\) (at room temperature), 180 °C, 9 h.
Fig. S10 The GC spectra of liquid products after the reaction of methanol with CO and H\textsubscript{2} catalyzed by Ru-Co catalyst. Reaction conditions: 7.5 \textmu{}mol Ru(acac)\textsubscript{3} and 45 \textmu{}mol CoBr\textsubscript{2}, 3 mmol LiI, 2 mL DMI, 3.2 mmol methanol, 0.5 MPa CO and 5 MPa H\textsubscript{2} (at room temperature), 180 \textdegree{}C, 9 h.
**Fig. S11** Effect of CO pressure on the ethanol formation in the reaction of (CH₂O)ₙ with CO and H₂. Other conditions were the same as that of entry 1 in Table 1.
Fig. S12 The GC spectra of (a) liquid sample and (b) gaseous sample after the CO₂ hydrogenation. Reaction conditions: 7.5 μmol Ru(acac)₃ and 45 μmol CoBr₂, 3 mmol LiI, 2 mL DMI, 3 MPa CO₂ and 5 MPa H₂ (at room temperature), 180 °C, 9 h.
**Fig. S13** The GC spectra of (a) liquid sample and (b) gaseous sample after the CO hydrogenation. Reaction conditions: 7.5 μmol Ru(acac)$_3$ and 45 μmol CoBr$_2$, 3 mmol LiI, 2 mL DMI, 0.7 MPa CO and 5 MPa H$_2$ (at room temperature), 180 °C, 9 h.
Fig. S14 The GC spectra of (a) liquid sample and (b) gaseous sample after the CO hydrogenation. Reaction conditions: 7.5 μmol Ru(acac)$_3$ and 45 μmol CoBr$_2$, 3 mmol LiI, 2 mL DMI, 3 MPa CO and 5 MPa H$_2$ (at room temperature), 180 °C, 9 h.