Electronic Supplementary Information

Synthesis of ethanol from paraformaldehyde, CO₂ and H₂

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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 $(CH_2O)_n$ with CO_2 and H_2 . Reaction conditions were the same as that of entry 1 in Table 1.



Target 1







Target 3



Fig. S2 The GC-MS spectra of the liquid product after the reaction of $(CH_2O)_n$ with CO_2 and H_2 . Reaction conditions were the same as that of entry 1 in Table 1.



Target 1



Target 2



(replib) Ethanol





Fig. S3 The GC-MS spectra of reaction solution using $({}^{13}CH_2O)_n$ instead of $(CH_2O)_n$. 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 $(CH_2O)_n$ and C of CO_2 , respectively. 2. According to fragment analysis, the C atom of CH_3 group in ethanol product was from $(CH_2O)_n$.





Fig. S4 The ¹H NMR (a) and ¹³C NMR (b) spectra of reaction solution using $(CH_2O)_n$, and the ¹H NMR (c) and ¹³C NMR (d) spectra of reaction solution using $(^{13}CH_2O)_n$. Reaction conditions were the same as that of entry 1 in Table 1.

Notes: From the ¹H NMR spectra (c) of the ¹³C-labelled reaction, it can be seen that the proton signal of CH₃ group on the ethanol product splits into three peaks compared to the standard spectra (a), which is caused by the coupling with ¹³C atom. From the ¹³C NMR spectra (d) of the ¹³C-labelled reaction, it can be observed that the C signal of CH₃ group was abnormally high in contrast to the standard spectra (b). In addition, the C signal of CH₂ group splits into triple peaks, which is caused by the coupling with the adjacent ¹³C atom in the CH₃ group. Both ¹H NMR and ¹³C NMR spectra confirmed that the C atoms of CH₃ group in ethanol product are mostly from $(CH_2O)_n$.



Target 2



Target 3



Fig. S5 The GC-MS spectra of reaction solution using $(CD_2O)_n$ instead of $(CH_2O)_n$. 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 D_2 instead of H_2 . Other reaction conditions were the same as that of entry 1 in Table 1.



Fig. S7 The GC spectra of reaction solution after hydrogenation of $(CH_2O)_n$ by Ru catalyst. Reaction conditions: 7.5 µmol Ru(acac)₃, 3 mmol LiI, 2 mL DMI, 3.2 mmol "CH₂O" monomer (0.1 g), 5 MPa H₂ (at room temperature), 180 °C, 1 h.



Fig. S8 The GC spectra of reaction solution after hydrogenation of $(CH_2O)_n$ by Co catalyst. Reaction conditions: 45 µmol CoBr₂, 3 mmol LiI, 2 mL DMI, 3.2 mmol "CH₂O" monomer (0.1 g), 5 MPa H₂ (at room temperature), 180 °C, 1h.



Fig. S9 The GC spectra of (a) liquid sample and (b) gaseous sample after the CO₂ hydrogenation catalyzed by Ru(acac)₃ catalyst. Reaction conditions: 7.5 μ mol Ru(acac)₃, 3 mmol LiI, 2 mL DMI, 3 MPa CO₂ and 5 MPa H₂ (at room temperature), 180 °C, 9 h.



Fig. S10 The GC spectra of liquid products after the reaction of methanol with CO and H_2 catalyzed by Ru-Co catalyst. Reaction conditions: 7.5 µmol Ru(acac)₃ and 45 µmol CoBr₂, 3 mmol LiI, 2 mL DMI, 3.2 mmol methanol, 0.5 MPa CO and 5 MPa H_2 (at room temperature), 180 °C, 9 h.



Fig. S11 Effect of CO pressure on the ethanol formation in the reaction of $(CH_2O)_n$ 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 CO_2 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 μ mol Ru(acac)₃ and 45 μ mol CoBr₂, 3 mmol LiI, 2 mL DMI, 0.7 MPa CO and 5 MPa H₂ (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 μ mol Ru(acac)₃ and 45 μ mol CoBr₂, 3 mmol LiI, 2 mL DMI, 3 MPa CO and 5 MPa H₂ (at room temperature), 180 °C, 9 h.