Electronic Supplementary Information

Efficient Synthesis of Acetic Acid via Rh Catalyzed Methanol Hydrocarboxylation with CO$_2$ and H$_2$ at Milder Condition

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Fig. S1 The representative GC spectra of (a) liquid sample with internal standard toluene and (b) gaseous sample after methanol hydrocarboxylation with CO\textsubscript{2} and H\textsubscript{2}. Reaction conditions were the same as that of entry 1 in Table 1.
**Fig. S2** The GC-MS spectra of the liquid product. Reaction conditions were the same as that of entry 1 in Table 1.
Fig. S3 XPS spectra of 4-MI (a) and the complex formed by Rh₂(CO)₄Cl₂ and 4-MI (b).

Notes:
1. The coordination of Rh₂(CO)₄Cl₂ and 4-MI was conducted as follows: 0.0058 g Rh₂(CO)₄Cl₂ (30 μmol Rh) and 0.041 g 4-MI (0.5 mmol) were dissolved in 20 mL methanol, respectively. The above solutions were mixed and stirred for 5 hrs at 40 °C. Then diethyl ether (40 mL) was added in the reaction mixture to precipitate the target compound. After removing the solvent by centrifuging, the compound was washed with additional 40 mL diethyl ether for 2 times and dried under vacuum at 50 °C for 12 hrs before the XPS analysis.
2. The X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCA Lab 220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10⁻⁹ mbar. The binding energy was referenced to the C₁s line at 284.8 eV from adventitious carbon.
3. In Fig. S3a, the peak at 399.4 eV coincides with pyridinic N atom, and the peak at 400.5 eV coincides with pyrrolic N atom.
Fig. S4 The result of the recycling test. Reaction conditions were the same as that of entry 1 in Table 1.
Fig. S5 The GC spectra of liquid products with internal standard toluene after the reaction of methanol with CO and H₂. Reaction conditions: 30 μmol Rh₂(CO)₅Cl₂ (based on the metal), 0.5 mmol 4-MI, 4 mmol LiCl, 1 mmol Lil, 2 mL DMI, 12 mmol methanol, 5 MPa CO and 5 MPa H₂, 180 °C, 15 h.
Fig. S6 The GC spectra of (a) liquid products with internal standard toluene and (b) gaseous products after CO$_2$ hydrogenation. Reaction conditions: 30 μmol Rh$_2$(CO)$_4$Cl$_2$ (based on the metal), 0.5 mmol 4-MI, 4 mmol LiCl, 1 mmol LiI, 2 mL DMI, 5 MPa CO$_2$ and 5 MPa H$_2$, 180 ºC, 15 h.
Fig. S7 The GC-MS spectra of reaction solution using $^{13}$CH$_3$OH instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: The molecular weight of acetic acid formed in the reaction was 61 Daltons. This demonstrates that the two C atoms in the acetic acid product were from $^{13}$C of $^{13}$CH$_3$OH and C of CO$_2$, respectively.
Fig. S8 The GC-MS spectra of reaction solution using CH$_3^{18}$OH instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: The molecular weight of acetic acid synthesized was still 60 Daltons. This result supports two deductions.

1. The CH$_3$ and $^{18}$OH group broke away during the reaction. Otherwise, the molecular weight of acetic acid should be 62 Daltons.

2. The CO$_2$ directly participated in the reaction. If methanol carbonylation with CO dominated in the reaction, the $^{18}$OH group generated in situ would take part in the formation of acetic acid with the CH$_3$CORh*I intermediate and the molecular weight of acetic acid should be 62 Daltons, as discussed elsewhere.$^{1,2}$
Fig. S9 The GC-MS spectra of reaction solution using CH$_3$OD instead of methanol. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes: The molecular weight of acetic acid generated in the reaction was still 60 Daltons. This result supports three deductions.
1. The CH$_3$ and OD group broke away during the reaction. Otherwise, the molecular weight of acetic acid should be 61 Daltons.
2. The CO$_2$ directly participated in the reaction. If methanol carbonylation with CO dominated in the reaction, the OD group generated in situ would take part in the formation of acetic acid with the CH$_3$CORh*I intermediate and the molecular weight of acetic acid should be 61 Daltons, as discussed in the literature.\textsuperscript{1,2}
3. H atom in the COOH group of acetic acid was from the reactant H$_2$. Otherwise, the molecular weight of acetic acid should be 61 Daltons.
Fig. S10 The $^1$H NMR (a) and $^{13}$C NMR (b) spectra of reaction solution using methanol, and the $^1$H NMR (c) and $^{13}$C NMR (d) spectra of reaction solution using $^{13}$CH$_3$OH instead of methanol. Reaction conditions were the same as that of entry 1 in Table 1.

Notes: From the $^1$H NMR spectra (a, c), it can be seen that the proton signal of $^{13}$CH$_3$ group on the acetic acid molecule splits into two peaks by the coupling with $^{13}$C atom. From the $^{13}$C NMR spectra (b, d), it can be observed that the signal of carbonyl group became weaker and splits into dual peaks, which is caused by the coupling with the adjacent $^{13}$C atom in the $^{13}$CH$_3$ group. Both $^1$H NMR and $^{13}$C NMR spectra confirmed that the CH$_3$ group in acetic acid molecule is from methanol, i.e., CH$_3$ group of CH$_3$OH is transferred into the acetic acid product in the reaction.
References

1  Q. Qian, J. Zhang, M. Cui and B. Han, Nat. Commun., 2016, 7.