Supplementary Information (SI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2026

Supporting Information

Reductive Carbonylation of Ethylene with Simulated Flue Gas: In Situ CO_2 Capture and Conversion

Yuqi Yang, [a,b] Haozhi Zhou, [a,b] Xiaofang Liu *[a,c] and Hui Wang *[a,b,c]

a. CAS Key Laboratory of Low-carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China. E-mail: liuxiaofang@sari.ac.cn; wanghh@sari.ac.cn

b. Institute of Carbon Neutrality, ShanghaiTech University, Shanghai 201203, China

c. State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization

Table of Contents

1 Material and Methods

General

All operations involving air- or moisture-sensitive compounds were performed were carried out under inert atmosphere using schlenk techniques or in a glovebox. All commercially available reagents were used without further purification (unless otherwise noted). Among these, extra-dry solvents with water ≤ 50 ppm (by K.F.) were bought from Energy Chemical. And all reactions were carried out in a glass-lined stainless-steel reactor of 25 mL capacity equipped with a magnetic stirrer.

Prior to use, all glassware was dried in 80 °C, evacuated and refilled with argon at least three times.

Instrumentation

Gas chromatography

The liquid phase GC analysis was performed on Shimadzu-2014 with the FID detector and the Stabilwax®-DA column (60 m, 0.53 mm, 0.5 μm) which isothermally at 40 °C for 5 min, then heated to 300 °C at 20 °C min^{-1} for 13 min, held 1 min, $t_{r\ major}$ = 24 min. The gaseous mixture was collected and analyzed by gas chromatography equipped with thermal conductivity detector (Shimadzu GC-2014C) with Argon as the carrier gas.

The gas phase GC analysis was performed on Shimadzu-2014 with the TCD detector using argon gas as the carrier gas.

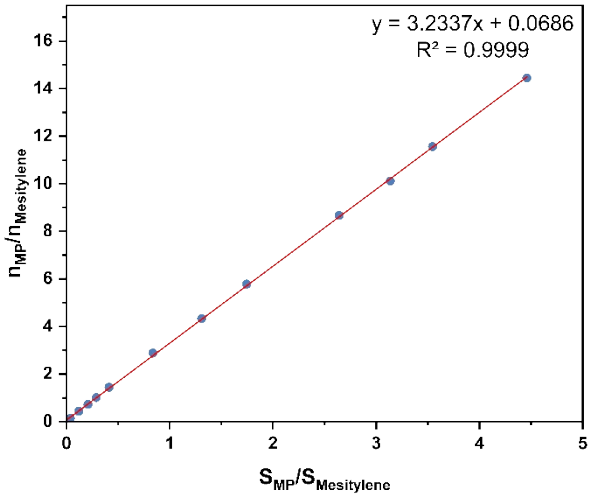
Mass Spectrometry

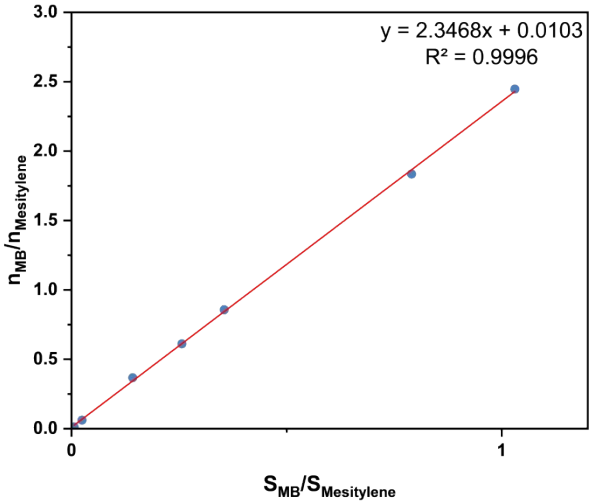
The samples were analyzed using a Waters Xevo G2-XS QTof high-resolution mass spectrometer with methanol as the diluent, operating in both positive ion mode (ESI^+) and negative ion mode (ESI^-).In positive ion mode (ESI^+), the settings were as follows: capillary voltage 3.0 kV, sampling cone voltage 40.0 V, source temperature 120 °C, desolvation temperature 250 °C, cone gas flow rate 100 L/h, and desolvation gas flow rate 700 L/h. In negative ion mode (ESI^-), the settings were as follows: capillary voltage 2.5 kV, sampling cone voltage 40.0 V, source temperature 100 °C, desolvation temperature 250 °C, cone gas flow rate 50 L/h, and desolvation gas flow rate 600 L/h.

GC-MS analysis was performed on PerkinElmer Clarus 680/SQ8T with the PerkinElmer Elite-5MSII column (30 m 0.25 mm 0.25 μm) which isothermally at 40 °C for 2 min, then heated to 250 °C at 15 °C min^{-1} for 14 min, held 5 min, $t_{r\ major}$ = 21 min. The detected mass is given in m/z units and is associated with the calculated mass of each species.

Calculation of the amount of product in the solution product

We quantified the solution from the reactor by the internal standard method (Mesitylene as the internal standard). Measure and plot the internal standard curve of methyl propionate (MP) and methyl butyrate (MB) relative to trimethylbenzene.





Typical procedure for methoxycarbonylation of ethylene with CO_2/MeOH

All reactions were carried out in a glass-lined stainless-steel reactor of 25 mL capacity equipped with a magnetic stirrer. Firstly, in the glove box, $Pd(OAc)_2$ (0.1 mmol), ligand (0.15 mmol) and MeOH (5 mL) were loaded into the container. The autoclave was sealed and purged three times with C_2H_4 gas, subsequently charged with C_2H_4 (5 bar), then CO_2 or simulated flue gas (35 bar) to total pressure of 40 bar. The autoclave was then heated at 140 °C for 12 h. After the reaction, the autoclave was cooled in the water bath and then the gas was vented into the gas collecting bag. The resulting solution was diluted with MeOH (10 mL) and added Mesitylene (100 μl) as internal standard. The sample was filtered through a short cotton plug, then analyzed by GC to determine the yields of the ester. Yields were found to be reproducible within Y = ±5 % in three independent runs for selected experiments.

During the in situ recycling tests, reactions were conducted in a 25 mL high-pressure reactor charged with MeOH and a CO_2/C_2H_4 gas mixture. After each reaction cycle, the gaseous products were released while retaining the liquid phase. The reactor was subsequently purged and recharged with the reaction gas mixture to 4 MPa for the next cycle. This procedure was repeated to evaluate the catalyst's performance under multiple in situ recycling conditions.

2 Figures and Tables

Figures

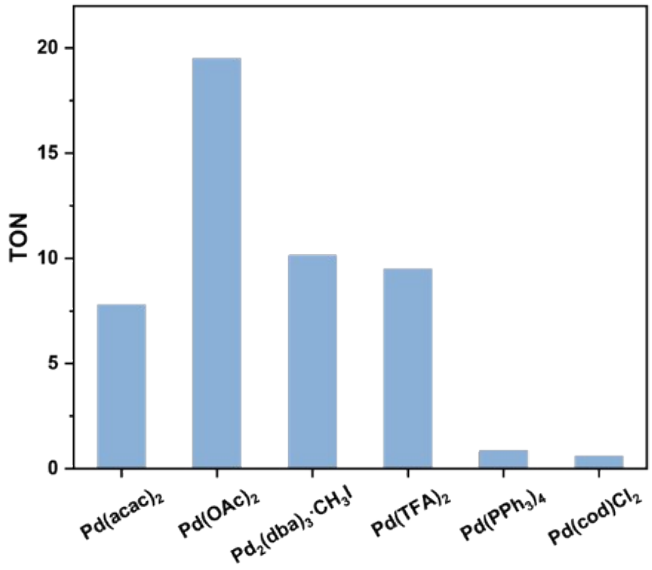


Fig. S1 The effect of Pd precursors on the catalytic performance of ethylene methoxycarbonylation.

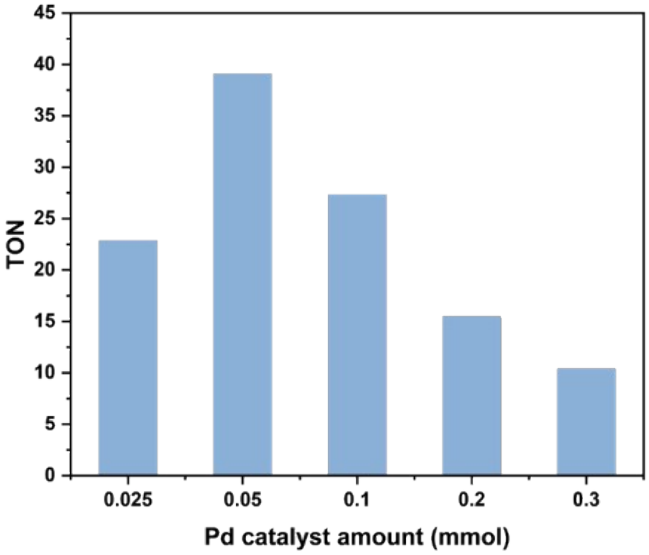


Fig. S2 The effect of Pd amount on the catalytic performance of ethylene methoxycarbonylation.

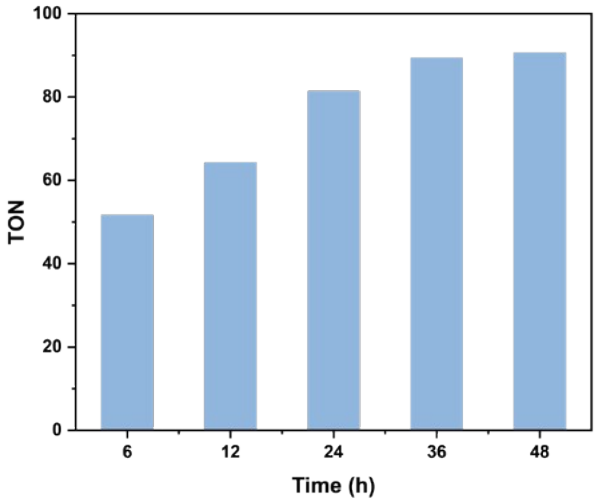


Fig. S3 Reaction progress over time.

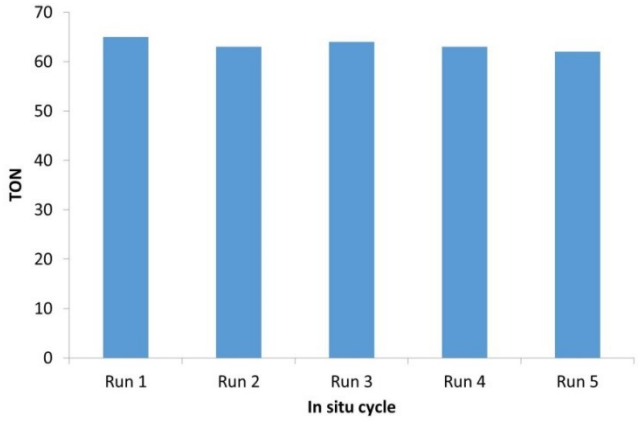


Fig. S4 The recycling test of the present catalytic system.

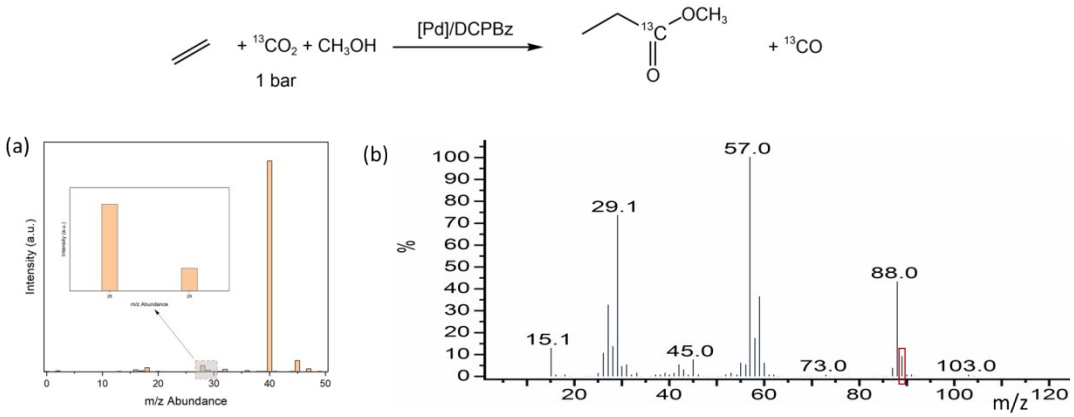


Fig. S5 Isotope experimental mass spectrometry data (a) gaseous phase (b) liquid phase.

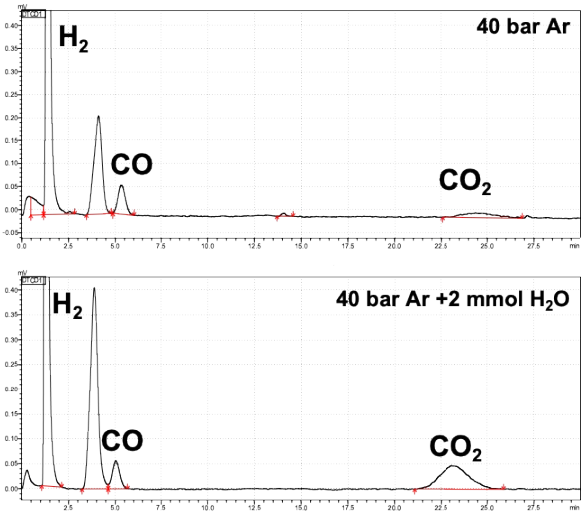


Fig. S6 Gas composition after methanol reaction under 40 bar Ar.

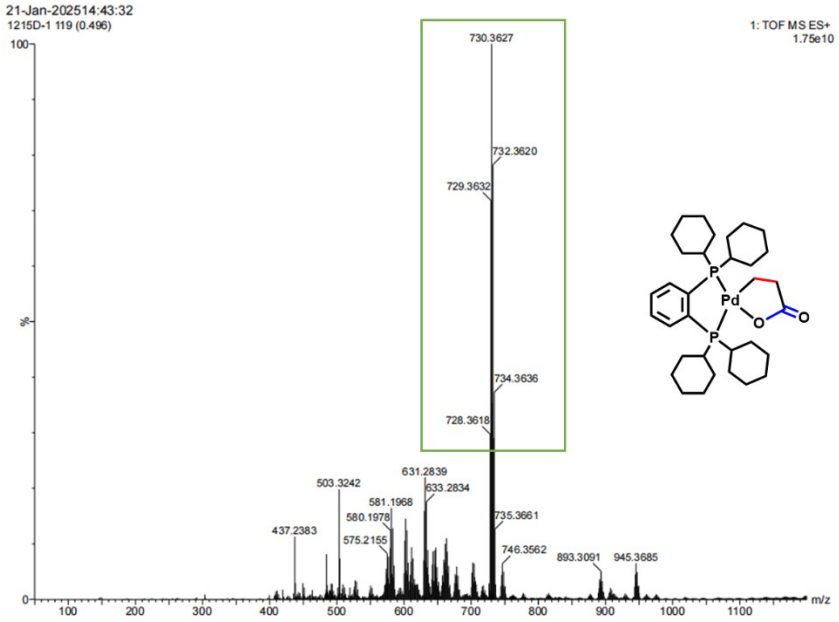


Fig. S7 ESI-MS data of the liquid phase after the reaction under standard conditions.

Table

Table S1 Representative catalytic systems for olefins carbonylation with CO_2 and clean reductant.

Entry	Catalytic system	Conditions	CO_2 source	TON	Ref.
1	Ru/[Bmim]Cl	160 °C, 40 bar CO_2	pure	12 (ethylene)	1
2	Ru-Co/[Bmim]Cl	160 °C, 40 bar CO_2	pure	93 (cyclohexene)	2
3	[Ru]@SILP-A-2/LiCl	160 °C, 40 bar CO_2	pure	94 (cyclohexene)	3
4	Ni/DCPBz	140 °C, 35 bar CO_2	pure	110 (ethylene)	4
5	Rh/PPh_3/p-TsOH	180 °C, 60 bar CO_2	pure	19 (cyclohexene)	5
6	IrI_4/LiI	170 °C, 50 bar CO_2	pure	86 (THF)	6
7	10Cu@SiO_2-PHM & Pd/Ph_2PPy/PTSA	400 °C, 5 bar CO_2 & ambient condition	diluted	99 (Phenylacetylene)	7
8	Pt@NaA & Pd/DTBPMB/PTSA	120 °C, 15 bar CO_2	pure	15 (1-hexene)	8
9	Ir/Pd/Zn$(OTf)_2$	120 °C, 20 bar CO_2	pure	26 (1-octene)	9
10	Pd/DCPBz	160 °C, 5 bar CO_2	diluted	89 (ethylene)	This work

Table S2 Influence of water on the performance of the catalytic system.

Entry[a]	Addition quantity of H_2O (mmol)	MP TON
1	-	64
2	0.2	72
3	2	61
4	20	5

[a] 0.05 mmol $Pd(OAc)_2$ and 0.05 mmol DCPBz dissolved in 5 mL MeOH; reaction in 25 mL stainless-steel reactor under 10 bar C_2H_4 and 30 bar simulated flue gas, 12 h.

Reference

1. L. Wu, Q. Liu, I. Fleischer, R. Jackstell and M. Beller, Nat. Commun., 2014, 5, 3091.

2. X. Zhang, C. Shen, C. Xia, X. Tian and L. He, Green Chem., 2018, 20, 5533-5539.

3. S.-P. Xia, G.-R. Ding, R. Zhang, L.-J. Han, B.-H. Xu and S.-J. Zhang, Green Chem., 2021, 23, 3073-3080.

4. Y. Yang, X. Liu, H. Zhou, J. Chen, Y. Lai, S. Zhang, H. Luo, H. Wang and Y. Sun, Green Chem., 2025, 27, 4706-4712.

5. T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer and W. Leitner, Angew. Chem. Int. Ed., 2013, 52, 12119-12123.

6. Y. Wang, Q. Qian, J. Zhang, B. B. A. Bediako, Z. Wang, H. Liu and B. Han, Nat. Commun., 2019, 10, 5395.

7. R. Sang, Y. Hu, R. Razzaq, G. Mollaert, H. Atia, U. Bentrup, M. Sharif, H. Neumann, H. Junge, R. Jackstell, B. U. W. Maes and M. Beller, Nat. Commun., 2022, 13, 4432.

8. D. De Vos, H. Van Dessel, S. Van Minnebruggen, J. Dedapper, P. Paciok, O. Usoltsev, A. Krajnc and A. Bugaev, Angew. Chem. Int. Ed., 2024, 64, e202418670.

9. M. N. Vellala Syed Ali, W. Huang, X. Tian, H. Jiao, R. Jackstell, R. Franke and M. Beller, J. Am. Chem. Soc., 2025, 147, 32873-32882.