

Supplementary information

Promoting nonsymmetric C–C coupling to valuable oxygenates without metal-catalysts in alkali aqueous medium

Peidong Zhu ^a, Chunling Wang ^{*a}, Heng Zhong ^a, Yang Yang ^a, Fangming Jin ^{*abc}

a. *School of Environmental Science and Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China;*

b. *Shanghai Key Laboratory of Hydrogen Science & Center of Hydrogen Science, Shanghai Jiao Tong University, Shanghai 200240, China*

c. *Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China*

*Corresponding author.

Email address: fmjin@sjtu.edu.cn (F. Jin); wangchunling@sjtu.edu.cn (C. Wang).

General Information

Materials

Sodium formate (HCOONa) and perchloric acid (HClO₄) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), magnesium hydroxide (Mg(OH)₂) and calcium hydroxide (Ca(OH)₂) were purchased from Alfa Aesar. Methanol (CH₃OH), ethanol (CH₃CH₂OH), propanol (CH₃CH₂CH₂OH), isobutyl alcohol ((CH₃)₂CHCH₂OH), sodium acetate (CH₃COONa), sodium propionate (CH₃CH₂COONa), and sodium isobutyrate ((CH₃)₂CHCOONa) were purchased from Sinopharm Chemical Reagent Co. LTD. Buffer solution was purchased from Panreac Química S. L. U. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Aladdin Biochemical Technology Co., Ltd. Nitrogen (N₂) and synthetic air were purchased from Air Liquide S.A. All chemical reagents and carrier gases were received and used without any other pretreatments.

Catalytic Testing

The HCOONa conversion was performed on a polytetrafluoroethylene (PTFE)-lined hydrothermal synthesis reactor. Typically, 10 mmol HCOONa, 10 mL H₂O and 1 mmol KOH were added into lining container, followed by ultrasonic blending, sealed and heat in oven at 250 °C for 3 h. After reaction finished, the autoclave was taken for naturally cooling to ambient temperature. Liquid samples were collected through a 0.45 μm PTFE syringe filter.

Liquid products C₁₋₄ alkanolic acids and C₁₋₄ alcohols were detected on high performance liquid chromatography (HPLC, Agilent 1200) and gas chromatography-flame ionization detector (GC-FID, Agilent 7890A), respectively. The HPLC measurements were carrying 2 mmol/L HClO₄ as mobile phase at a flow rate of 1.0 mL/min equipped with two KC-811 columns (SHODEX) and a UV/Vis absorbance detector set at 210 nm. The GC-FID system was using N₂ as carrier gas equipped with HP-INNOWAX capillary column.

The oxygenate selectivity mentioned in the paper is defined as follows:

$$\text{Oxygenate selectivity} = \frac{\text{specific oxygenate moles}}{\text{total oxygenate moles}} * 100\%$$

pH adjustments

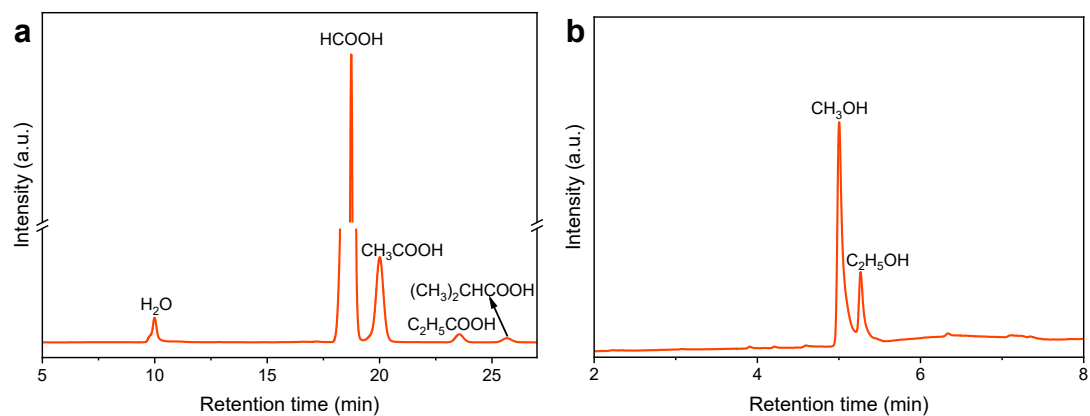
pH adjustments and measurements were operated on a Mettler Toledo Five Easy Plus pH meter. Prior to the test, pH meter was calibrated by buffer solutions of 4.0, 7.0 and 10.0. Therefore, we inspected pH value could affect C₂₊ synthesis. The pH values of pure HCOONa and HCOOH solution were 7.82 and 1.71, respectively, detected by pH-meter. We selected HCOOH or NaOH to adjust pH values of reaction solution under fixing 10 mmol carbon atoms (e.g., 1 mmol HCOOH + 9 mmol HCOONa).

Operando DRIFTS spectra

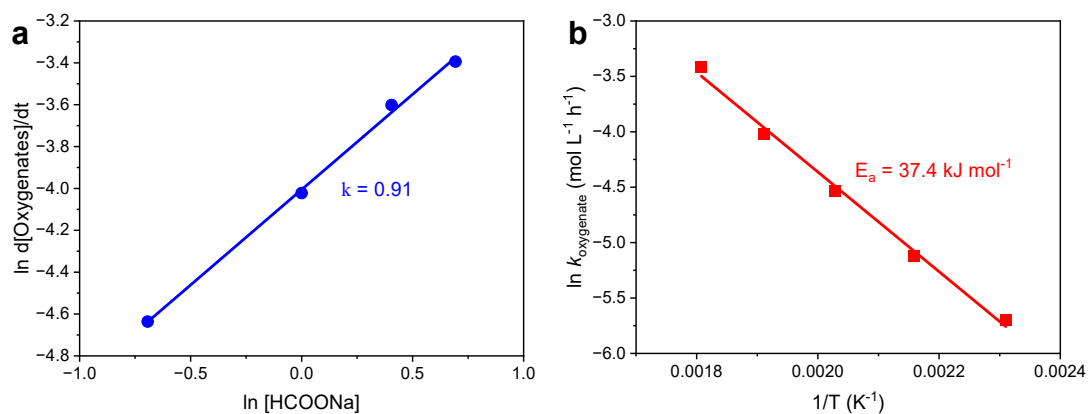
Operando DRIFTS was carried on a Thermo Fisher iS10 Fourier transform infrared spectroscopy (FTIR) spectrometer equipped with a high-temperature and high-pressure reaction cell. 1 M HCOONa solution was sealed in reactor and the input infrared ray could illuminate into chamber through diamond window on the reaction cell. After reaction solution absorbed, the output signal reached the detector via reflections.

In situ EPR measurements

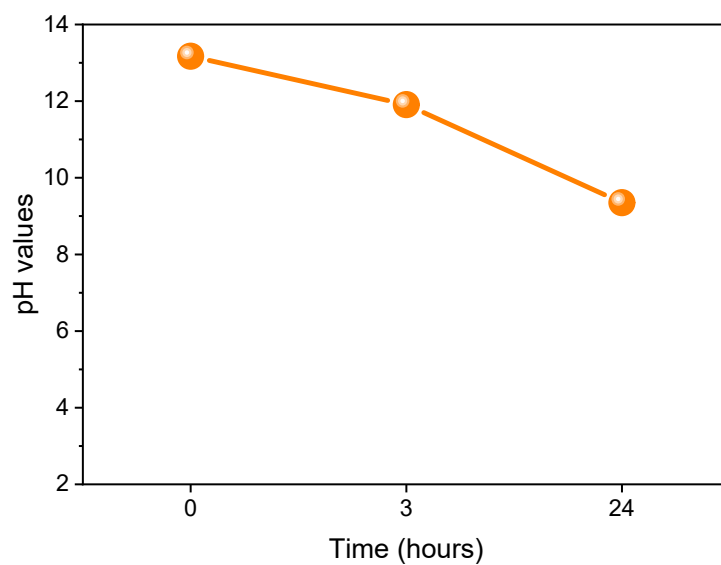
In situ EPR was conducted on a Bruker A300 device. Measuring parameters were listed as follows: microwave frequency, 9.85 GHz; microwave power, 20 mW; receiver gain, $2.5 \cdot 10^4$; center field, 3452 G; sweep width, 100 G; modulation frequency, 100 kHz; modulation amplitude, 2.0 G; time constant, 10 s; conversion time, 82 s; sweep time, 96 s; ten scans; temperature, 77 K. Prior to the test, 1 M HCOONa solution was added into a polytetrafluoroethylene (PTFE)-lined autoclave and sealed. Reaction temperature was elevated at a rate of 10 °C/min from 30 °C. Certain reaction solution (200 µL) was in situ taken and quickly mixed with a 100 µL DMPO (100 mM) solution. Above treated sample could be added into a capillary tube for the radical analysis.



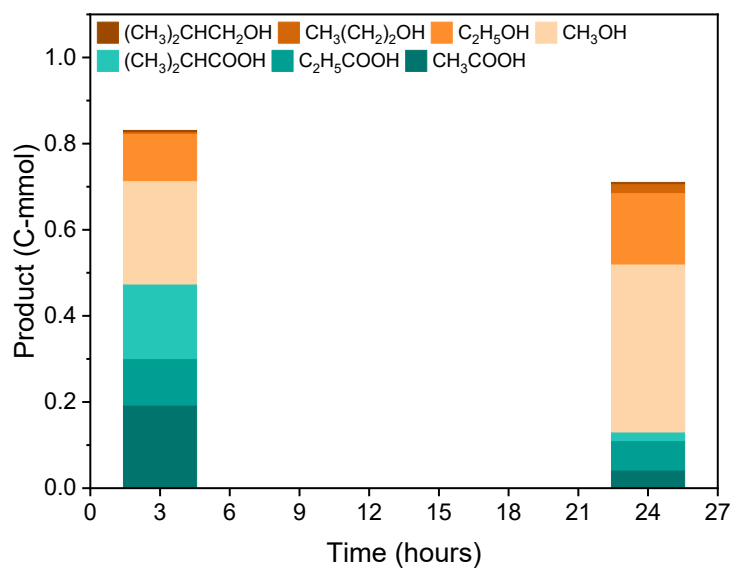
Supplementary Fig. 1. Chromatograms of detected products. (a) HPLC chromatogram of alkanolic acids. (b) GC-FID chromatogram of alkanolic alcohols. Reaction condition: 10 mmol HCOONa, 10 mL H₂O, 250 °C, 3 h.



Supplementary Fig. 2. Kinetic analysis of hydrothermal formate conversion to oxygenates. (a) Fitting plot of HCOONa concentration and logarithm of oxygenate production rate. Reaction condition: 10 mL H₂O, 250 °C, 3 h. (b) Arrhenius plot of reaction temperature and logarithm of oxygenate production rate. Reaction condition: 10 mmol HCOONa, 10 mL H₂O, 3 h.



Supplementary Fig. 3. Plots of pH values after reaction. Reaction condition: 10 mmol HCOONa, 1 mmol KOH, 10 mL H₂O, 250 °C.



Supplementary Fig. 4. Oxygenates yield after long reaction time. Reaction condition: 10 mmol HCOONa, 1 mmol KOH, 10 mL H₂O, 250 °C.

Supplementary Table 1 The solubility of different inorganic bases.

	KOH	NaOH	LiOH	Ba(OH) ₂	Ca(OH) ₂	Mg(OH) ₂
Solubility (g/g, 20 °C)	121	109	12.8	3.84	0.156	0.0009