

Supporting Information

A new strategy for CO₂ utilization with waste plastics: conversion of hydrogen carbonate into formate by polyvinyl chloride in water

Lihui Lu,^a Heng Zhong,^{b,c,d} Tianfu Wang,^{b,c} Jianeng Wu,^b Fangming Jin,^{*b,c,d} and Toshiaki

Yoshioka^{*a}

^a Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai, Miyagi 980-8579, Japan

^b School of Environmental Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan RD, Shanghai 200240, China

^c Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, P.R. China

^d Center of Hydrogen Science, Shanghai Jiao Tong University, No. 800, Dongchuan Road, Shanghai, 200240 China

*Corresponding authors:

fmjin@sjtu.edu.cn, Tel/Fax: +86-21-54742283.

yoshioka@env.che.tohoku.ac.jp, Tel: +81-22-795-7211, Fax: +81-22-795-7212.

1. Experimental section

1.1. Materials

PVC powder (Table S3) was purchased from Wako Pure Chemical Industries, Ltd. (Japan). NaHCO_3 (99.5%), NaOH (96%), KHCO_3 (99.5%), KOH (85%), Na_2CO_3 (99.8%), K_2CO_3 (99%), NaCl (99.5%), HCOONa (99.5%), dodecane (99%) and 1-dodecanol (99%) were purchased from National Drug Group Chemical Reagents Co. Ltd. (China). $\text{NaH}^{13}\text{CO}_3$ (99%) was purchased from Aldrich chemistry. In this research, different carbonates and hydrogen carbonates were used as the CO_2 source to simulate the CO_2 dissolving in alkaline solution, which is typically used for CO_2 capture, and to measure the amount of carbon reactant accurately.

1.2. Experimental procedures

All experiments were conducted in a batch tubular reactor (3/8 in. diameter, 1.24 mm wall thickness, and 120 mm length) made of stainless steel (SUS-316). In a typical experiment, 2.85 mL deionized water with test materials of PVC powder (2 mmol equivalent monomer of PVC) and NaHCO_3 were added into the reactor, which was then sealed and placed into an isothermal oven that had been preheated to a desired temperature. At desired reaction time, the reactor was removed from the oven and cooled in cold water bath (20°C) to terminate the reaction. The reaction time was defined as the time that the reactor was kept in the oven minus 30 min since it needed 30 min for the reactor to be heated to desired reaction temperature. Liquid sample was collected after filtration through a 0.45 μm syringe filter. Solid sample was washed with deionized water for several times and dried in vacuum oven before further analysis.

A formate yield was used to evaluate the reaction efficiency, which was defined as the molar ratio of the produced formate after reaction to the initial hydrogen carbonate or carbonate before the reaction

on carbon basis (Eq. (1)). The dechlorination ratio of PVC was defined as the molar ratio of NaCl after the reaction to the Cl atoms in the initial PVC (2 mmol) (Eq. (2)).

$$Yield_{formate} (\%) = \frac{n_{formate}}{n_{initial \text{ hydrogencarbonate or carbonate}}} \times 100\% \quad (1)$$

$$Dechlorination \ ratio (\%) = \frac{n_{NaCl}}{n_{Cl \text{ in the initial PVC}}} \times 100\% \quad (2)$$

1.3. Analytical methods

Formate concentration and Cl⁻ concentration in the liquid samples were analyzed by an Agilent 1200 high-performance liquid chromatography (HPLC) system equipped with two KC-811 columns, a tunable UV/Vis absorbance detector for formate detection, and a refractive index detector (RID) detector for Cl⁻ detection. The liquid samples were also analyzed by a gas chromatography-mass spectrometer (GC-MS) analyzer (Agilent 7890A GC system and Agilent 5975C inert XL MSD) and total organic carbon (TOC) analyzer (Multi N/C 3100, Germany). Liquid samples after isotopic reactions were analyzed by a nuclear magnetic resonance (NMR, Avance III 600 MHz, 298.0 K) analyzer. Solid samples were analyzed by elemental analysis (CHN-coder MT6) and FT-IR (NICOLET iS10).

2. Additional results

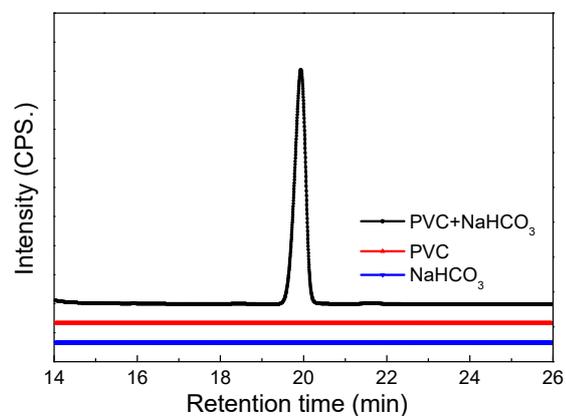


Fig. S1. HPLC chromatograms of liquid samples for reactions with different reactants (125mg PVC (2 mmol equivalent monomer), 3 mmol NaHCO₃, 2.85 mL deionized water, 300°C, 4 h).

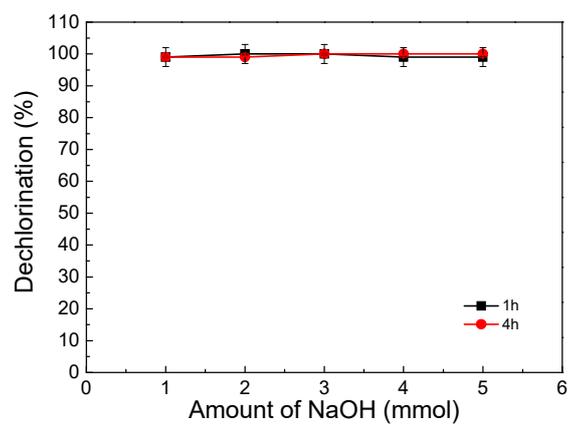


Fig. S2. Effect of different dosages of NaOH and NaHCO₃ on dechlorination of PVC (125mg PVC (2 mmol equivalent monomer), 1 mmol NaHCO₃, 2.85 mL deionized water, 300°C).

Table S1. Results of hydrogen carbonate conversion to formic acid/formate in the literature ^a

Entry	Carbon source	Hydrogen source	Metal/Catalyst	Formic acid/Formate Yield (%)	Other product
1	NaHCO ₃	H ₂ O	Fe ^{1,b}	1.8	--
2	NaHCO ₃	H ₂ O	Mg ^{1,b}	2.0	--
3	NaHCO ₃	H ₂ O	Zn ^{1,b}	36.2	--
4	NaHCO ₃	H ₂ O	Al ^{1,b}	15.0	--
5	NaHCO ₃	H ₂ (60 atm)	Ru-/Rh-phosphine complexes ²	Formate without yield ^c	--
6	NaHCO ₃	H ₂ (60 bar)	Fe-complexes ^{3,d}	86	--
7	NaHCO ₃	H ₂ (6 MPa)	NiNPore ^{4,b}	86.6	CH ₃ OH CH ₃ COOH
8	KHCO ₃	H ₂ O	Au-electrode ⁵	low	CO
9	NaHCO ₃	2-propanol	Ag/Cu ₂ O ^{6,e}	low	--

^a Compared to the literature¹⁻⁶, our work is proposed the concept of using PVC waste as the hydrogen source to reduce hydrogen carbonate to formate. Herein, we report NaHCO₃ reduction to formate by PVC with a 16% yield and nearly 100% selectivity based on hydrogen carbonate, simultaneously achieving the complete dechlorination of PVC in single step. The chemicals used in this work truly demonstrate ‘*green chemistry*’ without any toxic solvent, precious metal, elaborately-prepared catalysts and gaseous hydrogen. Moreover, the NaHCO₃ conversion efficiency in this work is much better than those by electro-/photo- chemical methods. ^b Reaction condition: under hydrothermal conditions. ^c Formate production was showed by formate concentration in the literature. ^d Fe-complexes: iron(II)-fluoro-tris-(2-(diphenylphosphino)phenyl)phosphino tetrafluoroborate. ^e Photocatalytic approach.

Table S2. Formate yield obtained with different amount of KHCO₃ and KOH ^a

Entry	KHCO ₃ (mmol)	KOH (mmol)	Formate yield (%) ^b
1	1	0	0
2	3	0	4.7
3	1	2	11.5
4	1	3	5.9
5	1	4	5.6

^a Reaction conditions: 125mg PVC (2 mmol equivalent monomer), 2.85 mL deionized water, 300°C and 4 h.

^b Results obtained from HPLC analysis.

Table S3. Properties of PVC material in this work

M_n^a (g·mol ⁻¹)	M_w^b (g·mol ⁻¹)	M_z^c (g·mol ⁻¹)	Dispersity (M_z/M_w)	Eff. Rad. ^e (nm)	Surface area (m/g)	Pore volume (DFT, cc/g) ^f
74,546	148,393	237,323	1.6	565.2	3.784	0.002

^a M_n : no. average molecular weight; ^b M_w : weight-average molecular weight; ^c M_z : z-average molecular weight. ^e Eff. Rad.: mean effective radius of particles. ^f DFT: density functional theory.

References:

1. F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei and R. L. Smith, *Energy Environ. Sci.*, 2011, **4**, 881-884.
2. F. Joó, G. Laurenczy, L. Nádasi and J. Elek, *Chem. Commun.*, 1999, **11**, 971-972.
3. C. Ziebart, C. Fedesel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 20701-20704.
4. T. Wang, D. Ren, Z. Huo, Z. Song, F. Jin, M. Chen and L. Chen, *Green Chem.* 2017, **19**, 716-721.
5. N. Sreekanth and K. L. Phani, *Chem. Commun.*, 2014, **50**, 11143-11146.
6. H. Pan, S. Chowdhury, D. Premachandra, S. Olguin and M. D. Heagy, *ACS Sustainable Chem. Eng.*, 2018, **6**, 1872-1880.