

Green Catalysis and Material Conversion Research Section

M. Tamura, Professor
 T. Nakajima, Associate Professor
 Y. Kita, Program-Specific Associate Professor
 P. Chen, Program-Specific Assistant Professor

1. Introduction

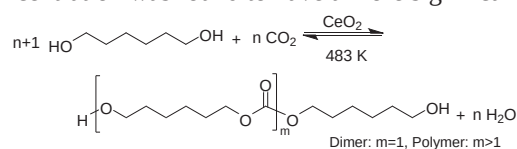
Our research group is developing catalytic technologies to advance carbon recycling as part of efforts to establish sustainable energy resource circulation systems. We focus on the design of novel catalysts, particularly heterogeneous catalysts, and their processes that enable the selective conversion of next-generation carbon resources, such as carbon dioxide, biomass, and plastics. In this year (2025), our research has concentrated on the development of effective catalyst reaction systems for polymer synthesis from CO₂ under ambient pressure, as well as the development of solid catalysts for the conversion of plastics into valuable chemicals. The details of these achievements are described below.

2-1. Development of a solid catalytic process for the direct synthesis of polycarbonate diols from CO₂ and diols under ambient pressure

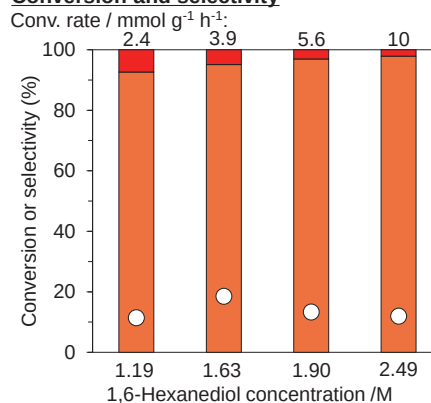
The development of technologies to reduce and utilize CO₂ is essential for addressing global warming and establishing a carbon-circulating society. In our laboratory, we focus on the chemical fixation of CO₂ and are developing solid catalytic technologies for polymer synthesis via the non-reductive transformation of CO₂. Our research group has found that cerium oxide (CeO₂) functions as an effective solid catalyst, enabling the selective synthesis of polycarbonate diols from CO₂ and diols by flowing CO₂ under ambient pressure. This reaction is severely limited by the equilibrium; in a closed system, the equilibrium yield is less than 0.1% at ambient CO₂, and the reaction hardly proceeds. In the catalytic system we developed, the water produced by the reaction is removed by distillation via CO₂ flow, thereby shifting the equilibrium toward the product side and allowing the reaction to proceed. However, from a practical perspective, the reaction rate is insufficient, and the reaction solvent poses issues for greenhouse gas (GHG) reduction. Therefore, we hypothesized that the solvent significantly affects the efficiency of water removal, and we aimed to construct a more efficient reaction system by clarifying the effects of solvent type and amount (substrate concentration).

Evaluation of the effects of Hansen solubility parameters and substrate concentration revealed that highly hydrophobic solvent systems (with higher

Hansen solubility parameters) provided higher activity, and that higher substrate concentrations also led to higher reaction rates. Fig. 1 shows the effect of the substrate concentration while keeping the Hansen solubility parameter constant, clearly indicating that higher substrate concentrations result in higher conversion. Among these parameters, substrate concentration was found to have a more significant



Conversion and selectivity



The correlation between 1,6-hexanediol concentration and conversion rate

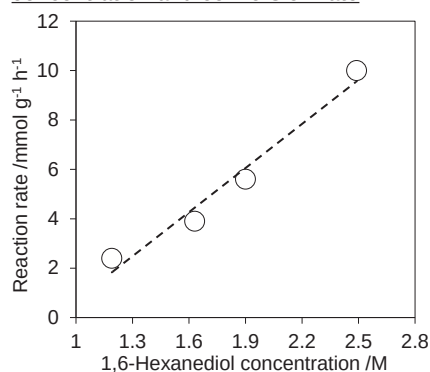


Fig. 1 Effect of the substrate concentration at the same Hansen solubility parameter ($R_a=35.5$) on the direct polymerization of flow CO₂ and 1,6-hexanediol. Reaction conditions: 1,6-hexanediol 0.5–2 g, CeO₂ 0.1 g, triglyme 1–3 g, diphenyl ether 0–4 g, and CO₂ 200 mL min⁻¹, 483 K, 2 h.

impact on the reaction rate, demonstrating that reducing the solvent amount can greatly enhance

catalytic performance.

Fig. 2 shows the time-courses of the reaction systems with reduced solvent amounts and under solvent-free conditions. The less solvent systems (i.e., higher substrate concentration) exhibit clearly higher reactivity, reaching high conversion in a shorter reaction time. In addition, the average molecular weight of the target polycarbonate diols was increased, demonstrating that it can also be controlled by adjusting the solvent amount.

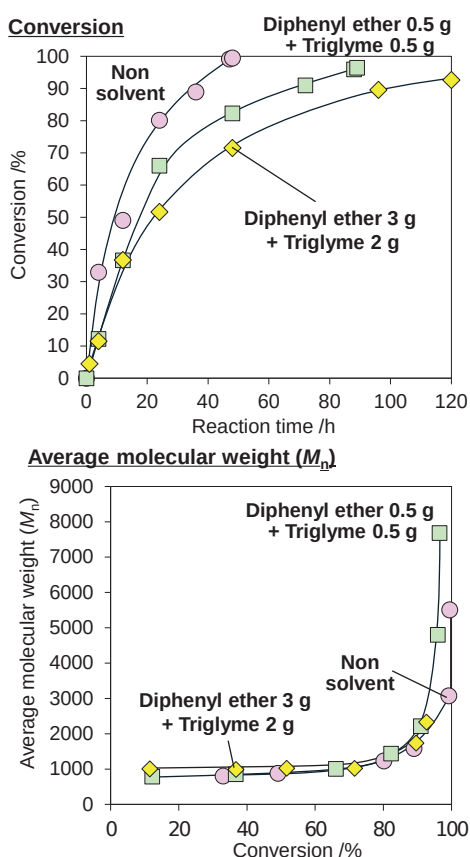


Fig. 2 Time-courses with different solvent conditions. Reaction conditions: 1,6-hexanediol 2 g (17 mmol), CeO_2 0.1 g, CO_2 flow rate 200 mL min^{-1} , 453 K.

2-2. Development of heterogeneous catalysts effective for the transformation of polyolefin plastics.

In recent years, plastic waste issues, including marine pollution and microplastics, have become increasingly evident, and the development of appropriate plastic waste management technologies has become an urgent priority. Furthermore, to realize a low-carbon society, implementing the 3R principles—reduce, reuse, and recycle—for plastics, which are valuable carbon resources, is essential. Our research group focuses on the chemical recycling of polyolefin plastics, which constitute the majority of plastic waste, and is developing heterogeneous catalysts that are effective for their conversion into valuable chemicals. To date, we have found that supported Ru catalysts exhibit high activity for the hydrogenolysis of

polyolefin plastics under relatively mild reaction conditions. In particular, Ru catalysts supported on CeO_2 and ZrO_2 (Ru/CeO_2 and Ru/ZrO_2) were found to suppress the formation of low-value gas products while yielding valuable liquid chemicals and waxes in high yields. However, to construct more efficient catalytic systems, further suppression of low-value gas products is required. Therefore, in this study, we aimed to reduce the formation of such gas products by controlling the size and surface composition of the active Ru metal sites.

During catalyst development, we found that reducing the Ru loading and introducing Cu into the Ru metal, forming a Cu–Ru/ CeO_2 catalyst, is effective for suppressing the formation of gas products. The catalyst structure and product yields under optimized conditions are shown in Fig. 3. Decreasing the Ru loading reduced the Ru particle size, and the introduction of Cu led to the formation of a surface Ru–Cu alloy. Consequently, the Ru ensemble size was decreased, leading to a suppression of gas formation.

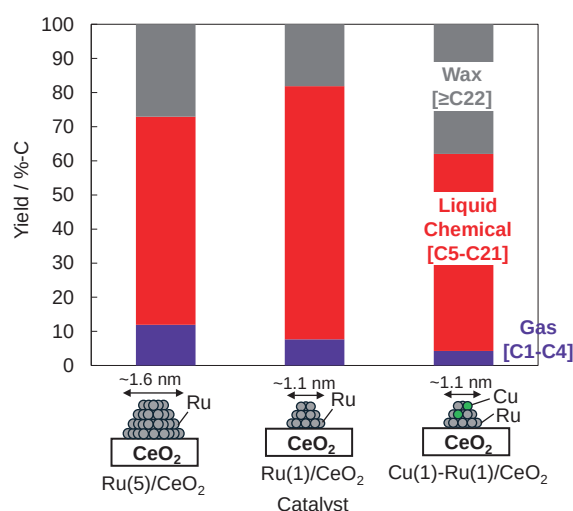


Fig. 3 Comparison of yields over various Ru catalysts under optimized conditions. Reaction conditions: LDPE 3.4 g, catalyst 0.2 g, H_2 5 MPa, 8–72 h, 453 K.

Acknowledgement

These works were supported by the Environment Research and Technology Development Fund (JPMEERF20223002) of the Environmental Restoration and Conservation Agency of Japan (ERCA), the JST CREST Grant Number (JPMJCR22L1) and the New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] M. Tamura, Y. Sasano, S.M.A.H. Siddiki, M. Akatsuka, P. Chen, and Y. Kita, *J. Catal.*, 452, 116417 (2025).
- [2] P. Chen, H. Lin, Y. Kita, K. Nakao, T. Arai, A. Nakayama, M. Tamura, *Energy Fuels*, 39, 20506–20516 (2025).

Collaboration Works

田村正純, Hanyang University (大韓民国), 二大学間共同研究 Graduate Program for Global Carbon Capture, Utilization, and Storage (G-CCUS)

Financial Support

1. Grant-in-Aid for Scientific Research

田村正純, 基盤研究(A), メタノールを炭素及び水素源とした非水素下でのバイオマス由来ポリオールの増炭反応

田村正純, 特別推進研究, 水素の活性化を駆動力とする次世代触媒反応の開発 (分担金)

中嶋隆, 基盤研究(B), 電極表面のガス種依存濡れ性制御による電解効率の飛躍的向上

喜多祐介, 基盤研究(B), ポリアミドのケミカルリサイクルを促進する不均一系触媒の開発

2. Others

田村正純, 国立研究開発法人科学技術振興機構 (CREST), バイオマス変換、樹脂分解触媒技術とLCA

田村正純, 国立研究開発法人科学技術振興機構 (CREST), ジオールと二酸化炭素を用いた PC 合成

田村正純, 三菱瓦斯化学株式会社, CO₂ 等を用いたプラスチック原料製造技術開発【研究開発項目 3】CO₂ からの機能性化学品製造技術の開発」におけるジフェニルカーボネートの製造研究にかかる共同研究

田村正純, 環境再生保全機構 (ERCA), プラスチック資源循環の展開とバイオ素材導入のための技術開発・政策研究

田村正純, 環境再生保全機構 (ERCA), ポリオレフィン系プラスチックのケミカルリサイクル技術の実証開発

中嶋隆, 若狭原子力技術シニアコンサルティング株式会社, パルスレーザーを使用した除染方法の最適化に関する研究

中嶋隆, 一般財団法人大成学術財団, 一般財団法人大成学術財団 (人体および環境への負荷を大幅に低減する粉塵計測支援パルスレーザー除染法の開発)

Publications

R. Kawaoto, T. Namba, Y. Ohtsuki, F. Yan, T. Nakajima, Predicting ablation-assisted nanosecond laser fabrication of glass optical diffusers by machine learning, *Results in Optics*, 21, 100865, 2025

M. Hirano, W. Onodera, M. Tamura, Y. Amao, Heterogeneous catalytic hydrogenation of *N*-benzyl nicotinamide: a comparative study with nicotinamide adenine dinucleotide, *Catalysis Science & Technology*, 15, 3806-3815, 2025

M. Hirano, W. Onodera, M. Tamura, Y. Amao, Highly selective 1,4-NADH regeneration via hydrogenated NAD⁺ analogs using a Pt/SiO₂ catalyst with low pressure hydrogen gas, *Chemical Communications*, 61, 16186-16189, 2025

M. Tamura, Y. Sasano, S. M. A. H. Siddiki, M. Akatsuka, P. Chen, Y. Kita, Chemical recycling of polyethylenes with low gas products by catalytic hydrogenolysis with heterogeneous CeO₂-supported Cu-doped Ru catalyst, *Journal of Catalysis*, 452, 116417, 2025

Y. Kita, A. Fukuda, P. Chen, M. Tamura, Poisoning effects of impurities on hydrogenolysis of polyethylenes over supported Ru catalysts, *Catalysis Today*, 461, 115492, 2025

P. Chen, H. Lin, Y. Kita, K. Nakao, T. Arai, A. Nakayama, M. Tamura, Direct Synthesis of Polycarbonate Diols with Tunable Molecular Weights from Atmospheric Flow CO₂ and Diols, *Energy & Fuels*, 39, 42, 20506-20516, 2025

Y. Kita, E. Sugimoto, M. Namba, P. Chen, M. Tamura, Synthesis of Low-Molecular-Weight Polyether Polyols by Self-Condensation of Diols over Amberlyst 15, *ACS Sustainable Chemistry & Engineering*, 14, 3047-3053, 2026

S. Mitsushima, T. Ioroi, Y. Kuroda, K. Nagasawa, T. Uchiyama, Y. Orikasa, H. Inoue, E. Higuchi, K. Ando, T. Nakajima, R. Misumi, Y. Uchimoto, Measurement Methods on Electrodes and Electrocatalysts for Water Electrolysis, *Electrochemistry*, 93, 4, 046001, 2025

田村正純, 触媒的ケミカルリサイクル技術の動向, 添加剤と高度プラスチックリサイクル, 53-63, 2025

田村正純, 触媒的変換によるポリオレフィン系プラスチックからの有用化学品合成, 日本包装学会誌, 34, 6, 343-354, 2025

Presentations

X. Li, Y. Kita, P. Chen, M. Tamura, Development of Cerium Oxide-Supported Ru-Based Bimetallic Catalysts

for Hydrogenolysis of LDPE under Low Pressure, 20th Japan-Korea Symposium on Catalysis, YONAGO CONVENTION CENTER “BIG SHIP”, 2025.5.20

D. Hong, M. N. Gebresillase, M. Tamura, J. Seo, Catalytic Dehydration of Primary Alcohols to Corresponding LAOs over Cmodified Al_2O_3 , 20th Japan-Korea Symposium on Catalysis, YONAGO CONVENTION CENTER “BIG SHIP”, 2025.5.20

Z. Peng, S. M. A. H. Siddiki, M. Akatsuka, P. Chen, Y. Kita, M. Tamura, Synthesis of Valuable Chemicals by Hydrogenolysis of Polyethylenes with Heterogeneous $\text{Ru}/\text{La}_2\text{O}_3\text{-CeO}_2$, 20th Japan-Korea Symposium on Catalysis, YONAGO CONVENTION CENTER “BIG SHIP”, 2025.5.21

藤井一輝, 荒井貴博, 佐藤啓, 中尾憲治, 田村正純, 藤埴大裕, 河瀬元明, CO_2 を原料としたポリカーボネートジオール合成のための気液固反応器の撹拌形式の検討, 石油学会 第 67 回年会 (第 73 回研究発表会), タワーホール船堀, 2025.5.26

秋山太一, 喜多祐介, 陳鵬茹, 田村正純, 担持ニオブ触媒によるアルコールを用いたアミンの *N*-アルキル化反応, 石油学会 第 67 回年会 (第 73 回研究発表会), タワーホール船堀, 2025.5.27

M. Tamura, Direct conversion of CO_2 and diols to polycarbonates over a heterogeneous CeO_2 catalyst, The 2nd KOREA-JAPAN Symposium on Chemistry AI for Carbon Neutrality 2025, INTERNATIONAL CONVENTION CENTER JEJU, 2025.6.4

M. Tamura, Heterogeneous Fe Catalysts for *N*-Alkylation of Amines with Alcohols, Taiwan International Conference on Catalysis, 国立清華大学, 2025.6.20

M. Tamura, Direct polymerization of CO_2 and diols using CeO_2 -based catalysts, 22nd International Conference on Carbon Dioxide Utilization, IST Congress Center, 2025.6.25

H. Lin, P. Chen, Y. Kita, A. Nakayama, M. Tamura, Direct synthesis of polycarbonate diols from flow CO_2 and diol over metal-modified CeO_2 catalysts, 22nd International Conference on Carbon Dioxide Utilization, IST Congress Center, 2025.6.26

林航昊, 陳鵬茹, 喜多祐介, 中山哲, 田村正純, Direct Polymerization of Atmospheric CO_2 and 1,6-Hexanediol over a Heterogeneous BaO -modified CeO_2 Catalyst, 第 14 回 JACI/GSC シンポジウム, 一橋大学, 2025.7.16

N. Uno, W. Onodera, P. Chen, Y. Kita, M. Tamura,

Hydrogenolysis of isosorbide to polyols over heterogeneous TiO_x -modified Rh catalysts, 10th ASIA-PACIFIC CONGRESS ON CATALYSIS, Suntec Singapore Convention and Exhibition Centre, 2025.8.5

T. Akiyama, Y. Kita, P. Chen, M. Tamura, Development of Nb-based heterogeneous catalysts for *N*-alkylation of amines with alcohols, 10th ASIA-PACIFIC CONGRESS ON CATALYSIS, Suntec Singapore Convention and Exhibition Centre, 2025.8.5

Y. Kita, T. Fukuda, P. Chen, M. Tamura, *N*-Alkylation of Amines with Alcohols over Fe-based Heterogeneous Catalysts, 10th ASIA-PACIFIC CONGRESS ON CATALYSIS, Suntec Singapore Convention and Exhibition Centre, 2025.8.7

田村正純, 金属酸化物の酸・塩基触媒機能を用いた液相有機合成反応, 第 19 回 触媒道場, 金沢, 2025.8.24

秋山太一, 喜多祐介, 陳鵬茹, 田村正純, アルコールを用いたアミンの *N*-アルキル化反応に有効な不均一系ニオブ触媒の開発, 第 136 回触媒討論会, 東北大学, 2025.9.17

宇野夏希, 小野寺渉, 陳鵬茹, 喜多祐介, 田村正純, イソソルビドの水素化分解によるポリオール合成用不均一系酸化チタン修飾ロジウム触媒の開発, 第 136 回触媒討論会, 東北大学, 2025.9.18

Z. Peng, S. M. A. H. Siddiki, M. Akatsuka, P. Chen, Y. Kita, M. Tamura, Hydrogenolysis of LDPE to value-added chemicals over $\text{La}_2\text{O}_3\text{-CeO}_2$ -supported Ru catalysts, 第 136 回触媒討論会, 東北大学, 2025.9.18

田村正純, 固体表面の酸・塩基点とその触媒機能, 近畿化学協会 触媒・表面部会 2025 年入門触媒化学セミナー, 大阪科学技術センター, 2025.10.7

M. Tamura, Catalytic conversion of polyolefins to valuable chemicals over heterogeneous Ru-based catalysts, JSPS Core-to-Core Program Japan-Southeast Asia, Joint Research Center for Plastic Resource Recycling, Penang, 2025.10.7

M. Tamura, Catalytic CO_2 conversion to valuable chemicals with a CeO_2 catalyst, International Symposium on Carbon Neutral Technology, Korea, 2025.10.28

田村正純, 二酸化炭素とジオールからの直接ポリカーボネート合成, 第 12 回 SPring-8 先端放射光技術による化学イノベーション研究会/第 113 回 SPring-8 先端利用技術ワーク, 品川, 2025.11.12

M. Tamura, Structure-activity relationship of Ru-based

catalysts in the hydrogenolysis of polyethylenes, JSPS Core-to-Core Program Japan-Southeast Asia, Joint Research Center for Plastic Resource Recycling, 大阪, 2025.12.1

M. Tamura, Synthesis of polyols from biomass-derived chemicals over heterogeneous catalysts, CCSIS Phnom Penh 2025, Cambodia, 2025.12.6

M. Tamura, Chemical upgrading of polyolefinic plastics by hydrogenolysis with heterogeneous catalysts, The International Chemical Congress of Pacific Basin Societies 2025, HAWAII CONVENTION CENTER, 2025.12.18

Z. Peng, S. M. A. H. Siddiki, M. Akatsuka, P. Chen, Y. Kita, M. Tamura, Synthesis of valuable chemicals by hydrogenolysis of polyolefins over a heterogeneous Ru/La₂O₃-CeO₂ catalyst, The International Chemical Congress of Pacific Basin Societies 2025, HAWAII CONVENTION CENTER, 2025.12.19

P. Chen, H. Lin, Y. Kita, M. Tamura, Direct synthesis of polycarbonate diols with high molecular weights from atmospheric flow CO₂ and diols over a CeO₂ catalyst, The International Chemical Congress of Pacific Basin Societies 2025, HAWAII CONVENTION CENTER, 2025.12.20

H. Lin, P. Chen, Y. Kita, A. Nakayama, M. Tamura, Development of metal oxide-modified CeO₂ catalysts for direct synthesis of polycarbonate diols from CO₂ and diols, The 3R International Scientific Conference on Material Cycles and Waste Management, Centara Grand at Central Plaza Ladprao Bangkok, 2025.12.20

田村正純, 二酸化炭素からのポリマー合成用固体触媒の開発, 産総研講演会 触媒化学研究部門の講演会, 産総研つくば, 2025.12.23

M. Tamura, P. Chen, Y. Kita, Chemical Transformation of Polyolefins to Valuable Chemicals by a Heterogeneous Cu-Ru/CeO₂ Catalyst, The 3R International Scientific Conference on Material Cycles and Waste Management, Centara Grand at Central Plaza Ladprao Bangkok, 2026.3.10

木津直翔, 平野誠人, 石田玉青, 田村正純, 天尾豊, 不均一系金属担持触媒を用いた低圧水素ガスによるニコチンアミド系補酵素の水素化, 日本化学会第 106 春季年会(2026), 日本大学, 2026.3.17