



Synthesis of ethylene urea using carbon-dioxide-adsorbed titanium–zirconium mixed oxides

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ABSTRACT

To address the increasing global levels of CO₂ emissions, it is necessary to develop efficient strategies that can convert CO₂ into useful chemicals such as carbonates, ureas, and carbamates. Hybrid systems that combine direct capture and subsequent utilization of CO₂ offer a unique emission-controlling pathway for achieving a carbon-neutral society. Ti–Zr mixed oxides could be ideal candidates for CO₂ adsorption owing to the high specific surface areas pore sizes. Therefore, in this study, metal oxides with desirable acid-base sites that is, Ti_xZr_(1–x)O₂ with different Ti/Zr ratios were synthesized using combined sol-gel and solvothermal methods and then utilized to adsorb and synthesize ethylene urea (EU), an important precursor of pharmaceuticals and agricultural products. The results indicated that the CO₂ adsorption capacity of TiO₂–ZrO₂ mixed oxides were higher than that of TiO₂ alone at 100 kPa and 25 °C, corresponding to their higher specific surface areas and pore volumes compared to their individual oxide counterparts. CO₂-adsorbed Ti_xZr_(1–x)O₂ was subsequently used as a CO₂ source to generate EU through a reaction with ethylenediamine (EDA) and 2-propanol. Notably, samples containing higher proportions of Zr–Ti_{0.3}Zr_{0.7}O₂ and ZrO₂ produced EU in significant amounts, owing to their acid-base bifunctionality. Overall, EU was synthesized using CO₂-adsorbed Ti_xZr_(1–x)O₂ as a CO₂ source and as an accelerator for reacting with EDA, without requiring high-pressure or high-purity CO₂.

Introduction

CO₂ emissions are a major contributor to global warming and climate change; therefore, the amount of CO₂ accumulated in the atmosphere must be urgently (Boot-Handford et al., 2014). Consequently, significant effort is being devoted to reducing CO₂ emissions using technologies such as carbon capture, utilization, and storage, which is considered a crucial tool in supporting clean energy transitions and reducing emissions from fossil-fuel-intensive sectors (Valluri et al., 2022). In particular, hybrid capture–utilization systems that combine direct capture and subsequent utilization of CO₂ as a carbonyl source offer a unique solution to emissions control, thereby helping realize a carbon-neutral society. The transformation of CO₂ into value-added products such as organic carbonates, carbamates, and ureas has been extensively studied (Bhanage et al., 2003; Tamura et al., 2014; Peng et al., 2021). There are two types of reactions for converting CO₂ into valuable chemicals: reductive conversion, which aims to produce CO, formaldehyde,

methanol, and hydrocarbons (Xie et al., 2020; Appel et al., 2013; Kondratenko et al., 2013), and non-reductive conversion, which involves the use of alcohols and amines to directly generate carbonates, carbamates, and urea derivatives by utilizing CO₂ as a carbonyl source (Peng et al., 2022; Peng et al., 2021; Tomishige et al., 2020; Olajire, 2018; Tomishige et al., 2020; Tomishige et al., 2019). Of the aforementioned value-added products, 2-imidazolidinone, also known as ethylene urea (EU), is the simplest cyclic urea derivative that can be produced via non-reductive conversion of CO₂ through a reaction between CO₂, alcohols and ethylenediamine (EDA) (Tomishige et al., 2020). EU has recently gained great attention due to its varied applications as intermediates for biologically active pharmaceutical compounds, such as the HIV protease inhibitors, DMP 323 and DMP 450 (Swain and Mohanty, 2019; Hodge et al., 1998).

Conventionally, the synthesis of EU typically involves oxidative carbonylation of 1,2-diamines and amino alcohols using reagents such as phosgene, urea, organic carbonates, or the combination of CO/O₂

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(Baba et al., 2002; Jagtap et al., 2008). However, the aforementioned synthesis techniques are intrinsically toxic and hazardous. From the environmental viewpoint, the most desirable approaches for EU synthesis are the reaction of high-pressure CO₂ with alcohols and amines in the presence or absence of a catalyst (Tamura et al., 2013; Wu et al., 2010; Bhanage et al., 2003) (Scheme 1). However, the need for high temperature and high-pressure CO₂ in this reaction, which entails energy-consuming processes such as desorption of the adsorbent-captured CO₂, and compression could limit its large-scale applications.

Therefore, novel development of a method to synthesize EU from low concentrations of CO₂, without the need for high pressure, compression, and purification must be developed. To address these challenges, our team has developed an alternative strategy to tackle these challenges, involving the one-time adsorption of CO₂ onto a solid material, specifically dual-function materials (DFMs). These materials can then subsequently release CO₂ into the reaction system to produce EU.

These materials contain a sorbent as well as a catalyst component, allowing it to both capture CO₂ and convert them to value-added products without an intensive energy process (Omodolor et al., 2020). The most studied reaction for the DFMs application to date is CO₂ methanation using noble metals, like ruthenium (Ru) and rhodium (Rh) (Bravo et al., 2019; Omodolor et al., 2020; Merkouri et al., 2021). However, metal oxides with desirable acid-base sites are promising candidates for capturing CO₂ and subsequently reacting with amines to directly generate EU. Consequently, TiO₂-based organic-inorganic hybrid materials have been synthesized by our group for the adsorptive removal of bisphenol A from water (Suzuki et al., 2022). TiO₂-P25, TiO₂, and Ti_xZr_(1-x)O₂ with high specific surface areas were synthesized using the sol-gel and solvothermal methods (Suzuki et al., 2022). Notably, mixing ZrO₂ with TiO₂ led to an increase in the specific surface area and amount of bisphenol A adsorbed by Ti_xZr_(1-x)O₂/2-naphthalene carboxylic acid.

However, there have been no reports on utilizing Ti_xZr_(1-x)O₂ in hybrid CO₂-capture-and-utilization systems, where it can serve as a CO₂ adsorbent as well as a reaction accelerator for converting CO₂ into EU. Ti_xZr_(1-x)O₂ possesses acidic and basic sites on its highly mesoporous surface and a high specific surface area, owing to its acidic TiO₂ and amphoteric ZrO₂ components (Suzuki et al., 2022). Therefore, Ti_xZr_(1-x)O₂ could be a possible candidate for producing useful compounds through combined CO₂ capture and utilization. Ti_xZr_(1-x)O₂ samples were synthesized and characterized, and their CO₂ adsorption properties were evaluated. Subsequently, EDA was reacted with CO₂-adsorbed Ti_xZr_(1-x)O₂, to produce EU, and the products were qualitatively and quantitatively assessed.

Experimental section

Reagents

Titanium (IV) isopropoxide (97 %) and zirconium propoxide (70 % in propanol), which were used in the synthesis, were purchased from Sigma-Aldrich. A 0.1 M potassium chloride solution was prepared by

diluting a 3.3 M potassium chloride (KCl) solution purchased from Kanto Chemical. Hexadecylamine (HDA) was purchased from Tokyo Chemical Industry. *tert*-Butanol (>99.0 %, Sigma-Aldrich), deionized water (18.2 MΩ cm), and pure ethanol (>99.7 %, Merck) were also used.

Synthesis of Ti_xZr_(1-x)O₂

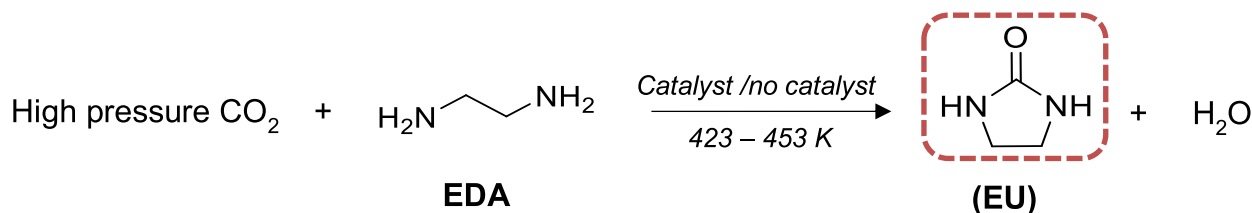
Mesoporous Ti_xZr_(1-x)O₂ specimens were synthesized using previously reported combined sol-gel and solvothermal process for different Ti/Zr ratios (Chen et al., 2012; Suzuki et al., 2022) (Figs. S1–2). For sample preparation by sol-gel, Titanium (IV) isopropoxide, HDA, and the KCl solution were mixed in ethanol, stirred for 2 h, and then stored for 24 h at room temperature. The precursor particles were subsequently obtained by centrifugation and drying. Thereafter, 1.6 g of the dried precursor particles, 20 mL of ethanol, and 10 mL of deionized water were mixed to initiate the solvothermal process and then heated at 160 °C for 24 h in an autoclave, followed by filtration and drying. TiO₂, Ti_{0.7}Zr_{0.3}O₂, Ti_{0.5}Zr_{0.5}O₂, Ti_{0.3}Zr_{0.7}O₂ and ZrO₂ and were synthesized using appropriate amounts of Titanium (IV) isopropoxide and zirconium propoxide following the same procedure. The resulting precursor particles were used to adsorb CO₂ and synthesize EU.

Procedure for CO₂ adsorption–desorption measurements

Ambient-pressure CO₂ adsorption isotherms were obtained using a BELsorp(II)-mini (BEL, Japan) adsorption instrument. All samples were pretreated at 200 °C under a vacuum. Adsorption experiments were performed using ultra high-purity CO₂ at pressures of 0–100 kPa at 25 °C, and the acquired data were fit to the Langmuir–Freundlich equation (Swenson and Stadie, 2019) to obtain CO₂ adsorption isotherms.

Procedure for synthesis of ethylene urea

To synthesize EU, 0.4 g of the previously synthesized CO₂-adsorbed Ti_xZr_(1-x)O₂ was mixed with 5 mmol of EDA and 25 mL of 2-propanol were placed in a Polytetrafluoroethylene (PTFE)-lined pressure-resisting acid digestion autoclave. The mixture was then stirred and heated at 160 °C for 24 h. Subsequently, the solution was filtered, and its components were analyzed by Gas Chromatography Mass Spectrometer equipped with flame ionization detector (GC–MS/FID; Agilent Technologies 8890 GC-system), with *tert*-butyl alcohol as an internal standard to determine the quality and quantity of the generated products. To quantify the amounts of the EU product and 2-piperazinone by-product, a calibration curve was obtained (Fig. S2) and Equations (S1 and S2) were utilized. Additionally, ¹H nuclear magnetic resonance spectroscopy (Bruker AV400; ¹H 400 MHz; solvent, D₂O; internal standard, *tert*-butyl alcohol) was conducted to confirm the structure of the produced EU. The GC chart and ¹H NMR spectrum of the reaction mixture is shown in (Figs. S3–6).



Scheme 1. Synthesis of ethylene urea (EU) using EDA and high-pressure CO₂ based on the conventional methods.

Results and discussion

CO₂-capturing capacity of Ti_xZr_(1-x)O₂

The adsorption of CO₂ onto TiO₂, Ti_{0.7}Zr_{0.3}O₂, Ti_{0.5}Zr_{0.5}O₂, Ti_{0.3}Zr_{0.7}O₂ and ZrO₂ up to partial pressures of 100 kPa was investigated. Isotherms describing the CO₂ adsorption onto the investigated samples were acquired (Fig. 1). At low pressures, there is a significant steepness observed for the isotherms for Ti_{0.3}Zr_{0.7}O₂ and ZrO₂, indicating enhanced interactions between these samples and CO₂ within their mesopores, potentially attributed to their reported acid-base characteristics, high specific surface areas and pore volume. The CO₂ adsorption capacity of the Ti_xZr_(1-x)O₂ mixed oxides was noticeably higher than that of only TiO₂ (0.278 mmol/g) and ZrO₂ (0.269 mmol/g). In particular, Ti_{0.3}Zr_{0.7}O₂ exhibited a 3.5 times higher adsorption amount (0.948 mmol/g) than that of TiO₂ or ZrO₂, whereas Ti_{0.5}Zr_{0.5}O₂ and Ti_{0.7}Zr_{0.3}O₂ absorbed 0.814 and 0.464 mmol/g of CO₂, respectively. As previously reported in the study by our group (Suzuki et al., 2022) and from the current characterization results (Fig. S8–9), TiO₂ exhibited CO₂ desorption at temperatures below 300 °C, while both Ti_xZr_(1-x)O₂ and ZrO₂ showed CO₂ desorption at temperatures above 550 °C as indicated by CO₂-temperature-programmed desorption (TPD) measurements (Fig. S9). The similarity in CO₂ desorption temperatures at higher temperatures for Ti_xZr_(1-x)O₂ and ZrO₂ suggests that the acid-base bifunctionality of these mixed oxides plays a role in their CO₂ adsorption capabilities. This study further indicated that mixed oxides of Ti and Zr exhibited higher specific surface areas and pore volumes compared to their individual oxide counterparts (Table S2).

To accurately determine the amount of CO₂ required for synthesizing EU, adsorption–desorption isotherm measurements were performed to evaluate the residual amount of CO₂ adsorbed on the surface at atmospheric pressure. A representative CO₂ adsorption–desorption isotherm of Ti_{0.3}Zr_{0.7}O₂ is presented in Fig. 2; the isotherms of all the other samples are shown in Fig. S7. Under this condition, Ti_{0.3}Zr_{0.7}O₂ and ZrO₂ were found to exhibit the highest (0.638 mmol/g) and lowest (0.269 mmol/g) amounts of CO₂ adsorbed onto their surfaces.

Moreover, the absence of overlap between the two isotherms in all samples indicates that the process of CO₂ adsorption and desorption is not reversible under the conditions studied, which is likely due to the strong interactions between the CO₂ molecules and the surface base sites.

Synthesis of EU from EDA and CO₂

EU was successfully produced using all the investigated samples through the reaction between CO₂-adsorbed Ti_xZr_(1-x)O₂ and EDA (Fig. 3). Additionally, 2-piperazinone was produced as a by-product. Notably, samples containing higher proportions of Zr—Ti_{0.3}Zr_{0.7}O₂ (0.128 mmol) and ZrO₂ (0.113 mmol) produced significantly higher amounts of EU (Fig. 3). This is consistent with the view that the by-functionality brought by the addition of ZrO₂ to TiO₂ in Ti_xZr_(1-x)O₂ can efficiently accelerate the reaction of CO₂ and EDA in the synthesis of EU. Additionally, the higher specific surface area and surface basicity of Ti_{0.3}Zr_{0.7}O₂ than those of Ti_{0.7}Zr_{0.3}O₂ and Ti_{0.5}Zr_{0.5}O₂, which has been previously reported by our group (Suzuki et al., 2022) (Table S2), is suspected to have induced strong interactions with the reactants and accelerated the reaction for synthesizing EU.

We postulate that in this reaction system, the Ti_xZr_(1-x)O₂ carbamate complex is directly formed without the formation of dicarbamic acid due to the absence of additional CO₂. The presence of 2-propanol as a basic solvent facilitates proton transfer and enables the reaction between ethylene carbonate and urea. This mechanism differs from the CeO₂ catalytic system, where the oxygen atom in CeO₂ acts as the proton acceptor, promoting the nucleophilic attack of the amine on the carbonyl carbon of ethylene carbonate (Peng et al., 2021) (Koizumi et al., 2021).

The efficiency of Ti_xZr_(1-x)O₂ as a hybrid material with two functionalities: as a CO₂ adsorbent and as a source of CO₂ in the synthesis of EU through its reaction with EDA and 2-propanol. A comparison was conducted between the post-reaction solutions obtained when using CO₂-adsorbed Ti_{0.3}Zr_{0.7}O₂ and those obtained from CO₂-free Ti_{0.3}Zr_{0.7}O₂ (Fig. 4). This comparison involved analyzing and comparing the total ion chromatograms (TIC) derived from GC–MS/FID measurements, which corresponded to the amount of EU produced in each case (Fig. 4).

As evidenced by significant differences in the peak areas in the FID chromatograms, CO₂-adsorbed Ti_{0.3}Zr_{0.7}O₂ produced more EU than CO₂-free Ti_{0.3}Zr_{0.7}O₂. Interestingly, even in the absence of CO₂ adsorption, Ti_{0.3}Zr_{0.7}O₂ could produce EU, albeit in smaller amounts, implying a possible interaction between ambient air CO₂ and EDA, or Ti_{0.3}Zr_{0.7}O₂ material owing to its acid-basic functionality. Overall, Ti_{0.3}Zr_{0.7}O₂ demonstrated efficacy in EU production without the need for high-pressure CO₂, and it synthesized EU directly without the formation of intermediate products.

To determine the optimal reaction temperature, a series of

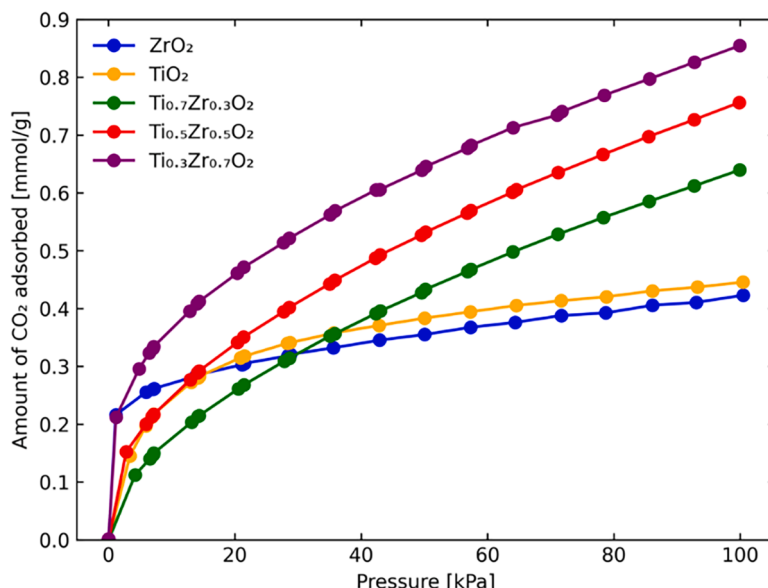


Fig. 1. CO₂ adsorption isotherms for ZrO₂ (blue), TiO₂ (orange), Ti_{0.3}Zr_{0.7}O₂ (purple), Ti_{0.5}Zr_{0.5}O₂ (red), and Ti_{0.7}Zr_{0.3}O₂ (green) at 25 °C.

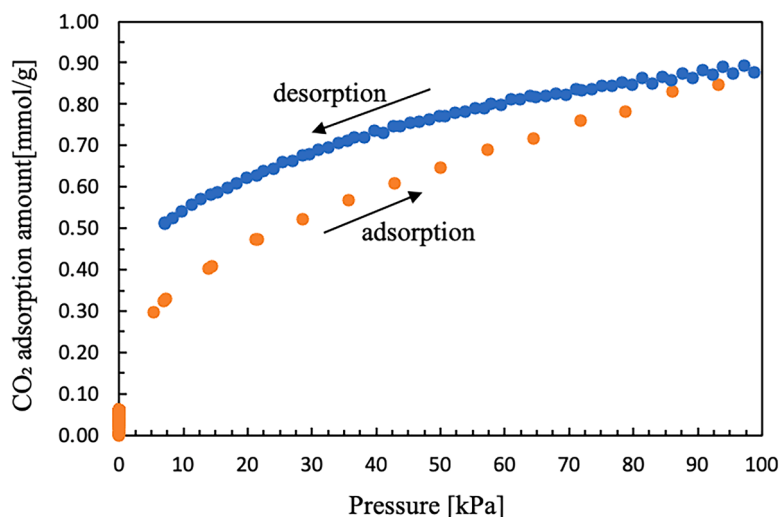


Fig. 2. CO₂ adsorption/desorption isotherm for Ti_{0.3}Zr_{0.7}O₂ acquired at 25 °C.

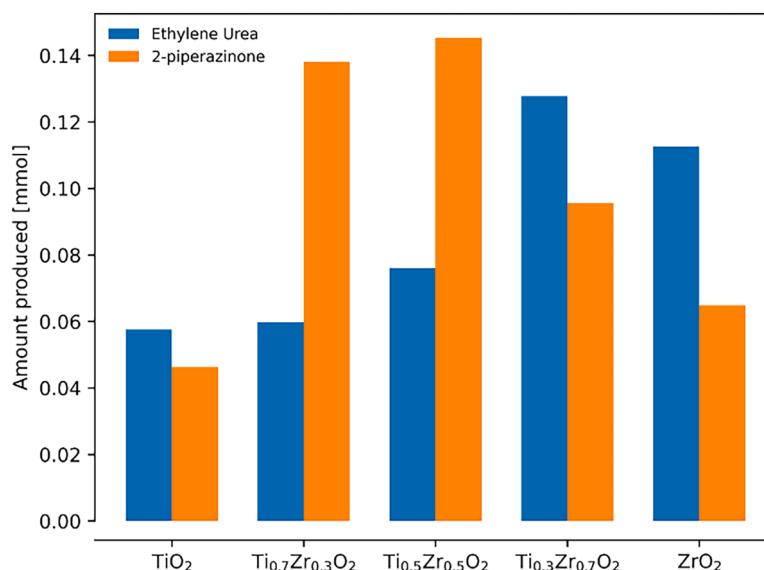


Fig. 3. Amounts of the EU product and 2-piperazinone by-product.

experiments were conducted at various temperatures (80–120 °C) for a 24-hr reaction period (Fig. 5). Given the higher CO₂ adsorption capacity and EU production observed in Ti_{0.3}Zr_{0.7}O₂ compared to other samples, it was chosen for subsequent experiments to examine the effects of reaction temperature on EU synthesis. A gradual increase in EU production was observed with an increase in temperature. Even at lower temperatures like 80 °C, albeit in smaller amounts, EU was still produced. However, a significant increase in EU production was observed from 100 to 160 °C, indicating that this temperature range can particularly be effective for EU production.

Future research and implications

This study highlights the potential ability of Ti_xZr_(1-x)O₂ as an effective CO₂ adsorbent and its subsequent use as a source of CO₂ to produce valuable compounds. While the Ti-Zr system showed promising results, exploring a wider range of other potential materials with similar characteristics that could provide a more comprehensive understanding of the CO₂ adsorption properties and efficiency. Future research could also focus on optimizing the synthesis parameters to enhance the CO₂

adsorption capacity and selectivity of the materials. This may involve investigating various synthesis techniques, doping strategies, or support materials to improve the performance.

Conclusions

This study has highlighted the remarkable capability of Ti_xZr_(1-x)O₂ as a CO₂ adsorbent and then as a CO₂ source for producing valuable compounds without requiring a pure, high-pressure CO₂ supply. Ti_xZr_(1-x)O₂ was successfully used in a combined CO₂-capture-and-conversion system to yield EU. Using combined sol-gel and solvothermal methods, Ti_xZr_(1-x)O₂ precursor samples with different Ti/Zr ratios exhibiting enhanced CO₂ adsorption capacity were synthesized. The adsorption capacity increased with increasing Zr content owing to the increase in surface area and basic site exposure. In particular, CO₂-adsorbed Ti_{0.3}Zr_{0.7}O₂ exhibited optimal behavior in terms of supplying CO₂ to synthesize EU.

Furthermore, an investigation of the effect of the reaction temperature on EU production suggested that although a high temperature (160 °C) produced the highest amount of EU, lower temperatures (100–140

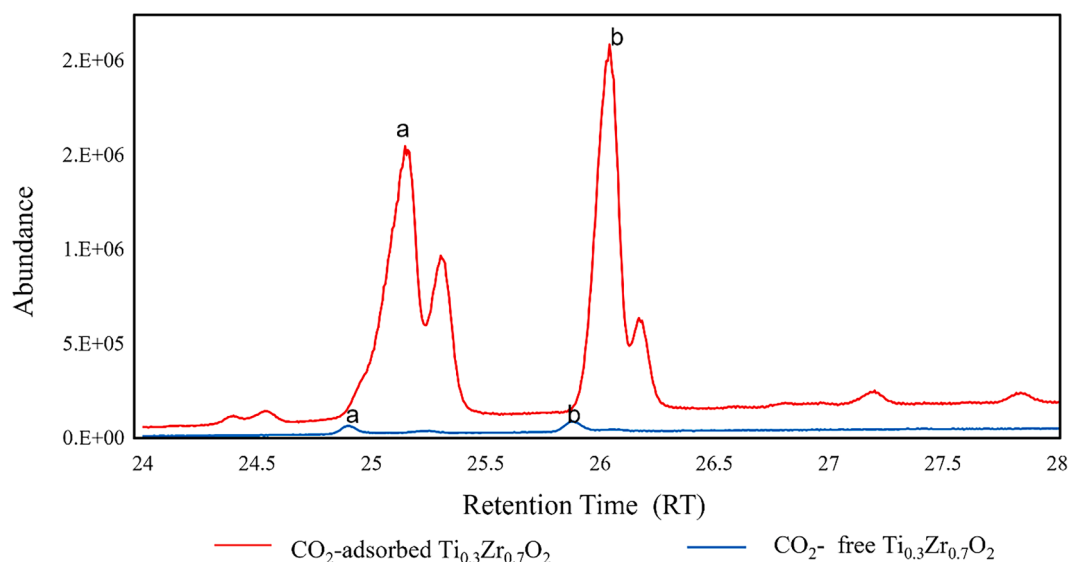


Fig. 4. FID-GC-MS-derived TICs for post-reaction solutions for each sample. Red (CO_2 -adsorbed $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_2$), blue (only $\text{Ti}_{0.3}\text{Zr}_{0.7}\text{O}_2$ without CO_2), *a* = (EU peak), *b* = (2-Piperazinone peak).

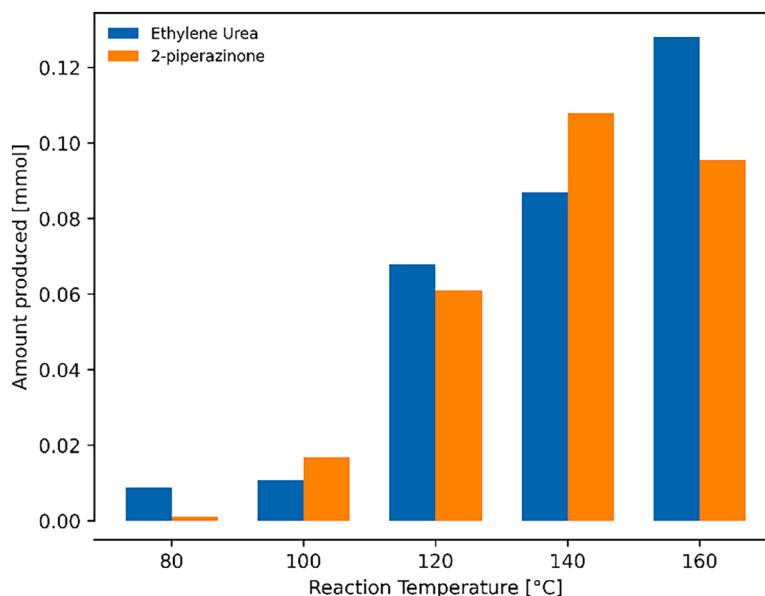


Fig. 5. The amount of EU and 2-piperazinone produced at different reaction temperatures.

°C) also generated EU in noteworthy amounts, underlining the energy-saving feature of our strategy for potential large-scale applications. This approach can be adopted to implement reaction systems that can convert CO_2 into useful compounds such as EU using metal oxides with specific properties. This study offers a viable energy-efficient method for alleviating climate change and reducing the atmospheric greenhouse gas content, which can help realize a carbon-neutral society.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Fiona Motswaiso: Writing – original draft, Visualization, Validation, Methodology, Investigation. **Ukyo Suzuki:** Methodology, Investigation, Conceptualization. **Kyosuke Sawaguchi:** Methodology,

Investigation, Conceptualization. **Farzana Rahman:** Writing – review & editing, Methodology, Investigation. **Tomohito Kameda:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Shogo Kumagai:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Yuko Saito:** Writing – review & editing, Supervision, Project administration. **Toshiaki Yoshioka:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.envc.2024.100970](https://doi.org/10.1016/j.envc.2024.100970).

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