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

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ARTICLE INFO

ABSTRACT

To address the increasing global levels of CO_2 emissions, it is necessary to develop efficient strategies that can convert CO_2 into useful chemicals such as carbonates, ureas, and carbamates. Hybrid systems that combine direct capture and subsequent utilization of CO_2 offer a unique emission-controlling pathway for achieving a carbon-neutral society. Ti-Zr mixed oxides could be ideal candidates for CO_2 adsorption owing to the high specific surface areas pore sizes. Therefore, in this study, metal oxides with desirable acid-base sites that is, $Ti_xZr_{(1-x)}O_2$ 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 CO_2 adsorption capacity of TiO_2-ZrO_2 mixed oxides were higher than that of TiO_2 alone at 100 kPa and 25 °C, corresponding to their higher specific surface areas and pore volumes compared to their individual oxide counterparts. CO_2-adsorbed $Ti_xZr_{(1-x)}O_2$ was subsequently used as a CO_2 source to generate EU through a reaction with ethylenediamine (EDA) and 2-propanol. Notably, samples containing higher proportions of Zr-$Ti_{0.3}Zr_{0.7}O_2$ and ZrO_2 produced EU in significant amounts, owing to their acid-base bifunctionality. Overall, EU was synthesized using CO_2-adsorbed $Ti_xZr_{(1-x)}O_2$ as a CO_2 source and as an accelerator for reacting with EDA, without requiring high-pressure or high-purity CO_2.

Introduction

CO_2 emissions are a major contributor to global warming and climate change; therefore, the amount of CO_2 accumulated in the atmosphere must be urgently (Boot-Handford et al., 2014). Consequently, significant effort is being devoted to reducing CO_2 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 CO_2 as a carbonyl source offer a unique solution to emissions control, thereby helping realize a carbon-neutral society. The transformation of CO_2 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 CO_2 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 CO_2 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 CO_2 through a reaction between CO_2, 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/O_2

(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 CO_2 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 CO_2 in this reaction, which entails energy-consuming processes such as desorption of the adsorbent-captured CO_2, and compression could limit its large-scale applications.

Therefore, novel development of a method to synthesize EU from low concentrations of CO_2, 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 CO_2 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 CO_2 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 CO_2 and subsequently reacting with amines to directly generate EU. Consequently, TiO_2-based organic-inorganic hybrid materials have been synthesized by our group for the adsorptive removal of bisphenol A from water(Suzuki et al., 2022). TiO_2-P25, TiO_2, and $Ti_xZr_{(1-x)}O_2$ with high specific surface areas were synthesized using the sol-gel and solvothermal methods(Suzuki et al., 2022). Notably, mixing ZrO_2 with TiO_2 led to an increase in the specific surface area and amount of bisphenol A adsorbed by $Ti_xZr_{(1-x)}O_2$/2-naphthalene carboxylic acid.

However, there have been no reports on utilizing $Ti_xZr_{(1-x)}O_2$ in hybrid CO_2-capture-and-utilization systems, where it can serve as a CO_2 adsorbent as well as a reaction accelerator for converting CO_2 into EU. $Ti_xZr_{(1-x)}O_2$ possesses acidic and basic sites on its highly mesoporous surface and a high specific surface area, owing to its acidic TiO_2 and amphoteric ZrO_2 components(Suzuki et al., 2022). Therefore, $Ti_xZr_{(1-x)}O_2$ could be a possible candidate for producing useful compounds through combined CO_2 capture and utilization. $Ti_xZr_{(1-x)}O_2$ samples were synthesized and characterized, and their CO_2 adsorption properties were evaluated. Subsequently, EDA was reacted with CO_2-adsorbed $Ti_xZr_{(1-x)}O_2$, 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.
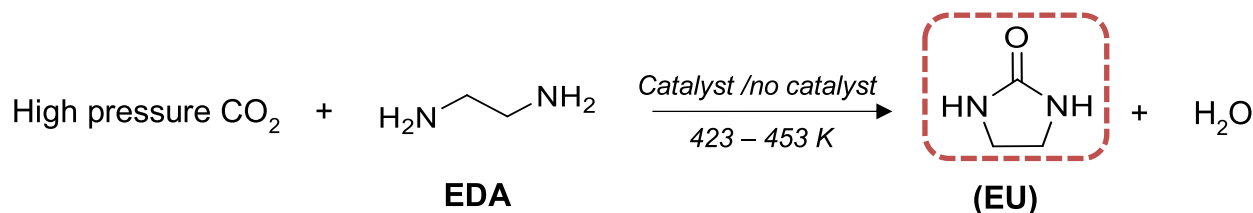
Synthesis of $Ti_xZr_{(1-x)}O_2$

Mesoporous $Ti_xZr_{(1-x)}O_2$ 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. TiO_2, $Ti_{0.7}Zr_{0.3}O_2$, $Ti_{0.5}Zr_{0.5}O_2$, $Ti_{0.3}Zr_{0.7}O_2$ and ZrO_2 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 CO_2 and synthesize EU.

Procedure for CO_2 adsorption–desorption measurements

Ambient-pressure CO_2 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 CO_2 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 CO_2 adsorption isotherms.

Procedure for synthesis of ethylene urea

To synthesize EU, 0.4 g of the previously synthesized CO_2-adsorbed $Ti_xZr_{(1-x)}O_2$ 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, ^{1}H nuclear magnetic resonance spectroscopy (Bruker AV400; [1]H 400 MHz; solvent, D_2O; internal standard, *tert*-butyl alcohol) was conducted to confirm the structure of the produced EU. The GC chart and ^{1}H NMR spectrum of the reaction mixture is shown in (Figs. S3–6).

Scheme 1. Synthesis of ethylene urea (EU) using EDA and high-pressure CO_2 based on the conventional methods.

Results and discussion

CO_2-capturing capacity of $Ti_xZr_{(1-x)}O_2$

The adsorption of CO_2 onto TiO_2, $Ti_{0.7}Zr_{0.3}O_2$, $Ti_{0.5}Zr_{0.5}O_2$, $Ti_{0.3}Zr_{0.7}O_2$ and ZrO_2 up to partial pressures of 100 kPa was investigated. Isotherms describing the CO_2 adsorption onto the investigated samples were acquired (Fig. 1). At low pressures, there is a significant steepness observed for the isotherms for $Ti_{0.3}Zr_{0.7}O_2$ and ZrO_2, indicating enhanced interactions between these samples and CO_2 within their mesopores, potentially attributed to their reported acid-base characteristics, high specific surface areas and pore volume. The CO_2 adsorption capacity of the $Ti_xZr_{(1-x)}O_2$ mixed oxides was noticeably higher than that of only TiO_2 (0.278 mmol/g) and ZrO_2 (0.269 mmol/g). In particular, $Ti_{0.3}Zr_{0.7}O_2$ exhibited a 3.5 times higher adsorption amount (0.948 mmol/g) than that of TiO_2 or ZrO_2, whereas $Ti_{0.5}Zr_{0.5}O_2$ and $Ti_{0.7}Zr_{0.3}O_2$ absorbed 0.814 and 0.464 mmol/g of CO_2, respectively. As previously reported in the study by our group (Suzuki et al., 2022) and from the current characterization results (Fig. S8–9), TiO_2 exhibited CO_2 desorption at temperatures below 300 °C, while both $Ti_xZr_{(1-x)}O_2$ and ZrO_2 showed CO_2 desorption at temperatures above 550 °C as indicated by CO_2-temperature-programmed desorption (TPD) measurements (Fig. S9). The similarity in CO_2 desorption temperatures at higher temperatures for $Ti_xZr_{(1-x)}O_2$ and ZrO_2 suggests that the acid-base bifunctionality of these mixed oxides plays a role in their CO_2 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 CO_2 required for synthesizing EU, adsorption–desorption isotherm measurements were performed to evaluate the residual amount of CO_2 adsorbed on the surface at atmospheric pressure. A representative CO_2 adsorption–desorption isotherm of $Ti_{0.3}Zr_{0.7}O_2$ is presented in Fig. 2; the isotherms of all the other samples are shown in Fig. S7. Under this condition, $Ti_{0.3}Zr_{0.7}O_2$ and ZrO_2 were found to exhibit the highest (0.638 mmol/g) and lowest (0.269 mmol/g) amounts of CO_2 adsorbed onto their surfaces.

Moreover, the absence of overlap between the two isotherms in all samples indicates that the process of CO_2 adsorption and desorption is not reversible under the conditions studied, which is likely due to the strong interactions between the CO_2 molecules and the surface base sites.

Synthesis of EU from EDA and CO_2

EU was successfully produced using all the investigated samples through the reaction between CO_2-adsorbed $Ti_xZr_{(1-x)}O_2$ and EDA (Fig. 3). Additionally, 2-piperazinone was produced as a by-product. Notably, samples containing higher proportions of Zr—$Ti_{0.3}Zr_{0.7}O_2$ (0.128 mmol) and ZrO_2 (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 ZrO_2 to TiO_2 in $Ti_xZr_{(1-x)}O_2$ can efficiently accelerate the reaction of CO_2 and EDA in the synthesis of EU. Additionally, the higher specific surface area and surface basicity of $Ti_{0.3}Zr_{0.7}O_2$ than those of $Ti_{0.7}Zr_{0.3}O_2$ and $Ti_{0.5}Zr_{0.5}O_2$, 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 $Ti_xZr_{(1-x)}O_2$ carbamate complex is directly formed without the formation of dicarbamic acid due to the absence of additional CO_2. 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 CeO_2 catalytic system, where the oxygen atom in CeO_2 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 $Ti_xZr_{(1x)}O_2$ as a hybrid material with two functionalities: as a CO_2 adsorbent and as a source of CO_2 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 CO_2-adsorbed $Ti_{0.3}Zr_{0.7}O_2$ and those obtained from CO_2-free $Ti_{0.3}Zr_{0.7}O_2$ (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, CO_2-adsorbed $Ti_{0.3}Zr_{0.7}O_2$ produced more EU than CO_2-free $Ti_{0.3}Zr_{0.7}O_2$. Interestingly, even in the absence of CO_2 adsorption, $Ti_{0.3}Zr_{0.7}O_2$ could produce EU, albeit in smaller amounts, implying a possible interaction between ambient air CO_2 and EDA, or $Ti_{0.3}Zr_{0.7}O_2$ material owing to its acid-basic functionality. Overall, $Ti_{0.3}Zr_{0.7}O_2$ demonstrated efficacy in EU production without the need for high-pressure CO_2, and it synthesized EU directly without the formation of intermediate products.

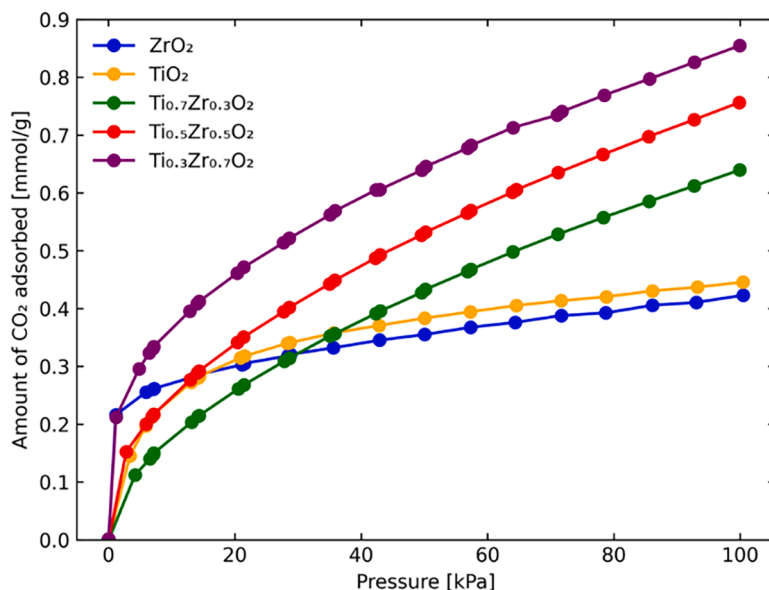To determine the optimal reaction temperature, a series of

Fig. 1. CO_2 adsorption isotherms for ZrO_2 (blue), TiO_2 (orange), $Ti_{0.3}Zr_{0.7}O_2$ (purple), $Ti_{0.5}Zr_{0.5}O_2$ (red), and $Ti_{0.7}Zr_{0.3}O_2$ (green) at 25 °C.
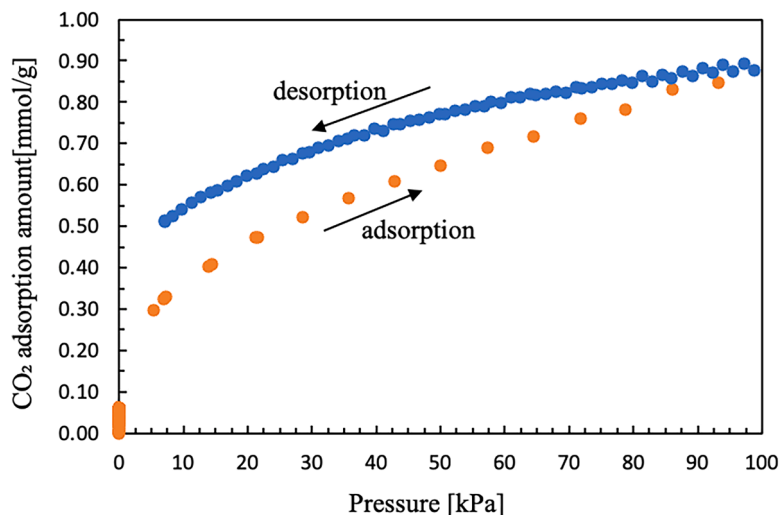
Fig. 2. CO_2 adsorption/desorption isotherm for $Ti_{0.3}Zr_{0.7}O_2$ acquired at 25 °C.
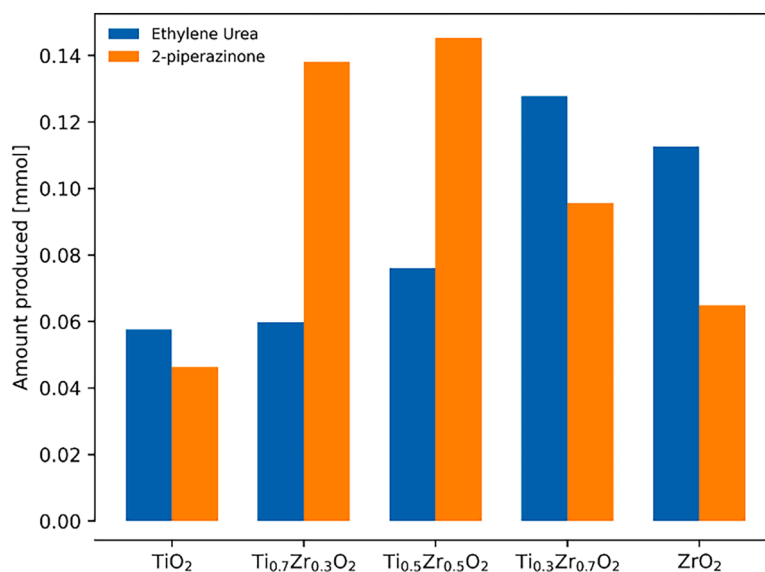

Fig. 3. Amounts of the EU product and 2-piperazinone by-product.

experiments were conducted at various temperatures (80–120 °C) for a 24-hr reaction period (Fig. 5). Given the higher CO_2 adsorption capacity and EU production observed in $Ti_{0.3}Zr_{0.7}O_2$ 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 $Ti_xZr_{(1-x)}O_2$ as an effective CO_2 adsorbent and its subsequent use as a source of CO_2 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 CO_2 adsorption properties and efficiency. Future research could also focus on optimizing the synthesis parameters to enhance the CO_2

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 $Ti_xZr_{(1-x)}O_2$ as a CO_2 adsorbent and then as a CO_2 source for producing valuable compounds without requiring a pure, high-pressure CO_2 supply. $Ti_xZr_{(1-x)}O_2$ was successfully used in a combined CO_2-capture-and-conversion system to yield EU. Using combined sol-gel and solvothermal methods, $Ti_xZr_{(1-x)}O_2$ precursor samples with different Ti/Zr ratios exhibiting enhanced CO_2 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, CO_2-adsorbed $Ti_{0.3}Zr_{0.7}O_2$ exhibited optimal behavior in terms of supplying CO_2 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
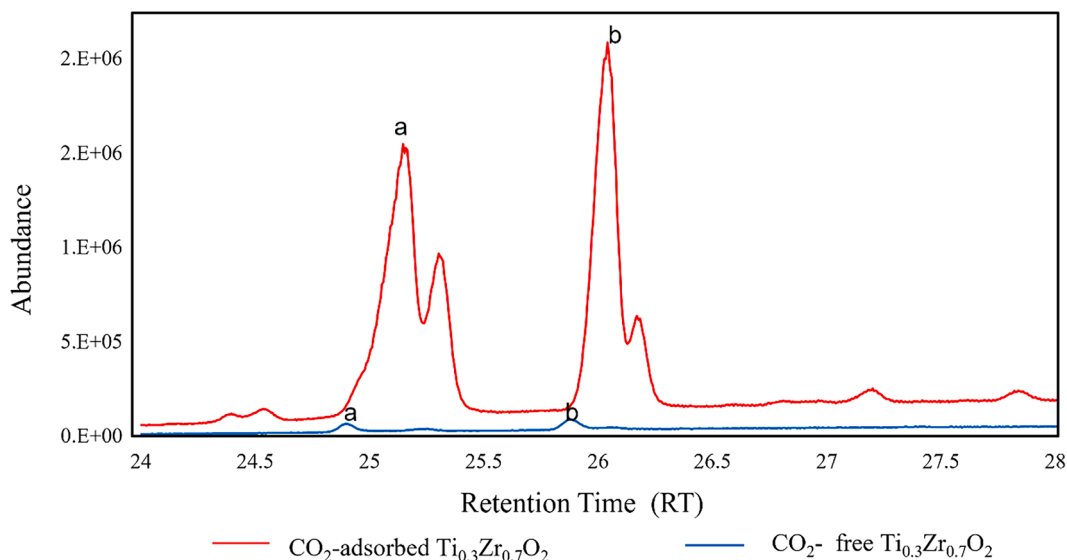
Fig. 4. FID-GC–MS-derived TICs for post-reaction solutions for each sample. Red (CO_2-adsorbed $Ti_{0.3}Zr_{0.7}O_2$), blue (only $Ti_{0.3}Zr_{0.7}O_2$ without CO_2), *a* = (EU peak), *b* = (2-Piperazinone peak).

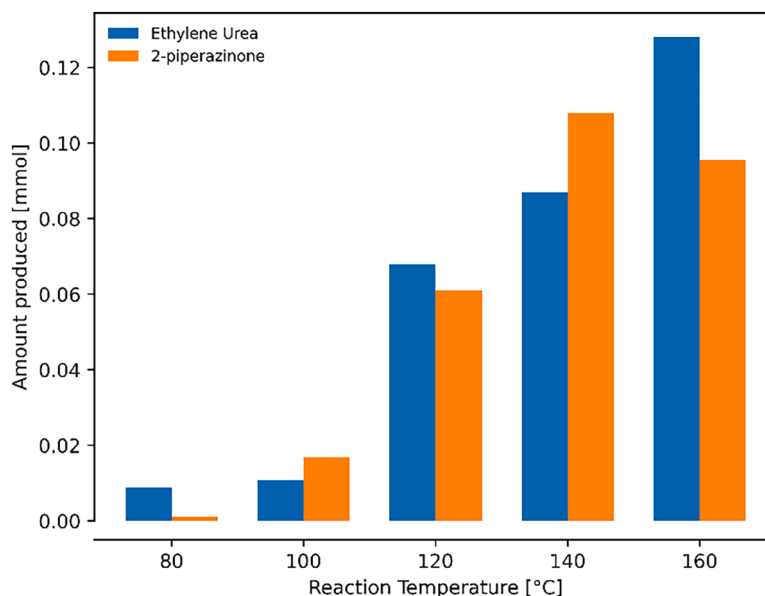**Fig. 5.** The amount of EU and 2-piperazinone produced at different reaction temperatures.

°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.

Acknowledgement

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envc.2024.100970.

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