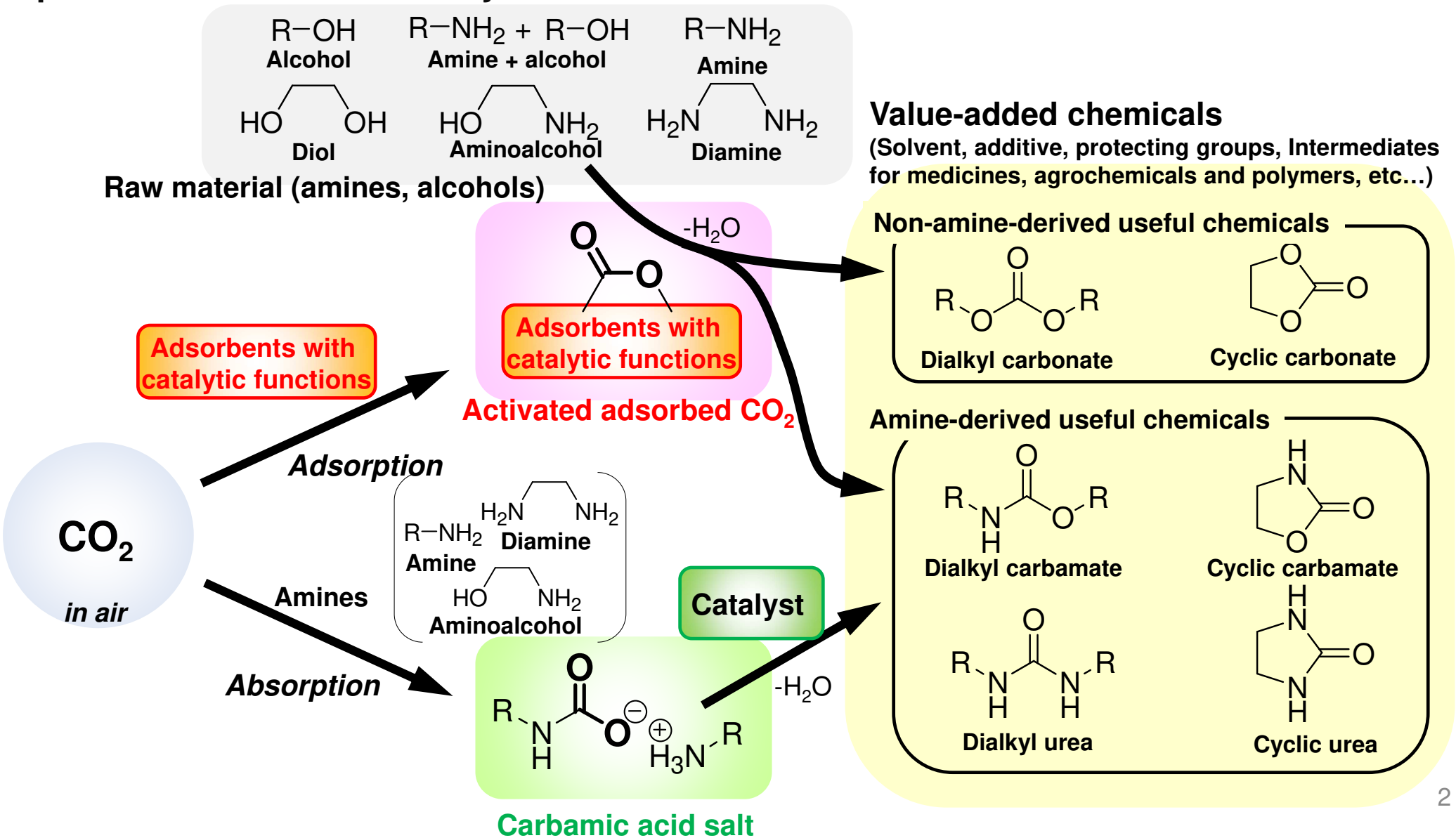
Development of Combined Carbon Capture and Conversion (quad-C) Systems for the Utilization of Atmospheric CO_2

Presenter : Masazumi Tamura (University Public Corporation Osaka (Osaka City University))
PM : Dr. FUKUSHIMA Yasuhiro, Tohoku University
Implementing organizations : Tohoku University, University Public Corporation Osaka (Osaka City University), Renaissance Energy Research Corporation

Development of reaction system ~ Development goal

Develop a reaction system for the direct synthesis of useful CO_2-derived chemicals (urea, organic carbonates, etc.) from CO_2-absorbed compounds (amines, etc.) or CO_2-adsorbed oxides (catalytic materials, LDH, etc.) without desorbing CO_2, and obtain knowledge for optimization of the reaction systems.

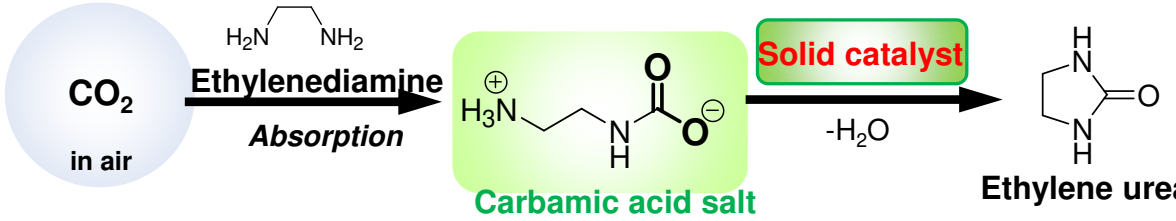


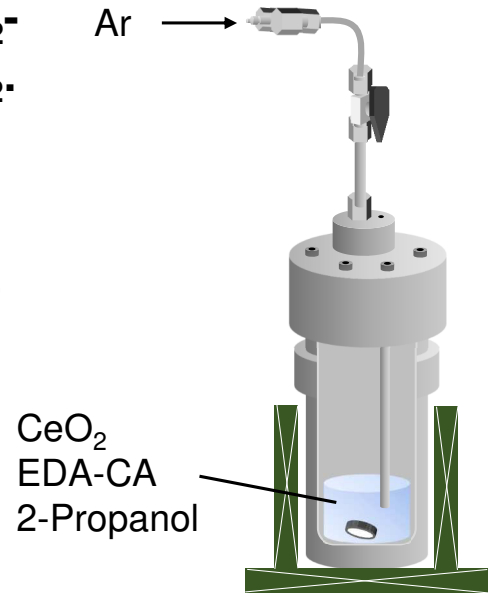
Development items, contents of study

(1) To develop effective solid catalysts for reaction systems that synthesize useful CO_2-derived chemicals (target products) from CO_2-absorbed compounds (such as amines) without once desorbing CO_2.

a) Exploration of catalysts and reaction conditions using ethylenediamine as a model substrate (Tohoku Univ.)

b) Characterization of catalyst structure, surface property and adsorbed species using Ethylenediamine as a Model Substrate (Osaka City Univ., Tohoku Univ.)



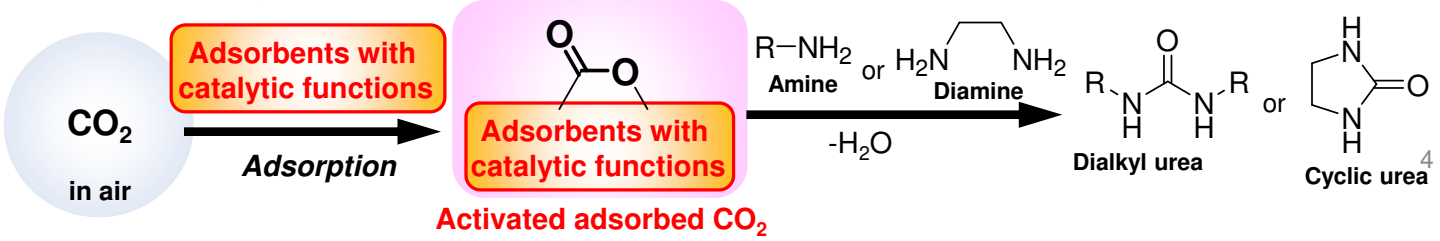


(2) To search for the oxides themselves and the substrates (amines, alcohols, etc.) to react with the adsorbed CO_2, and to develop an effective reaction system for the reaction system to synthesize useful chemicals (target products) from CO_2-adsorbed oxides (CeO_2-based catalysts) without once desorbing CO_2.

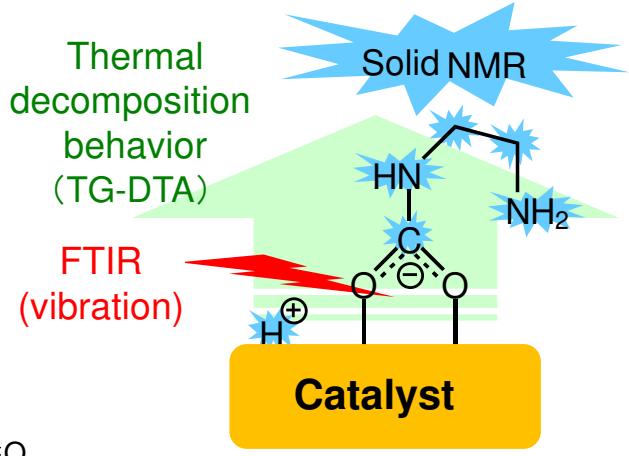
a) Analysis of adsorption behavior of CO_2 containing water vapor on oxides (Osaka City Univ.)

b) Reactions of adsorbed CO_2 with alcohols and amines (Tohoku Univ.)

c) Characterization of catalyst structure and surface property and analysis of adsorption state of CO_2 and reaction intermediates (Osaka City Univ., Tohoku Univ.)

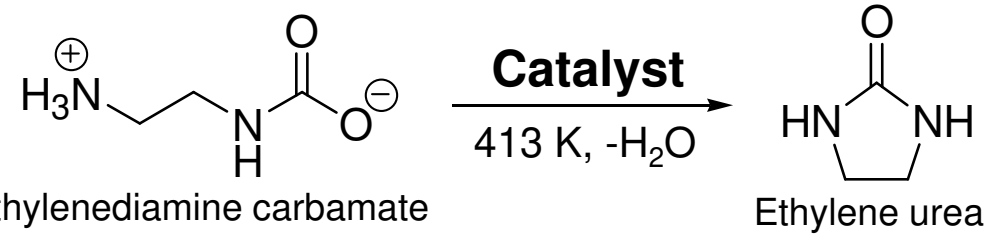


Approach for adsorbed EDA-CA



BET surface area/Pore distribution
XRD(bulk structure)
Temperature-programmed desorption (surface acid/base property)

Reaction and catalyst search results



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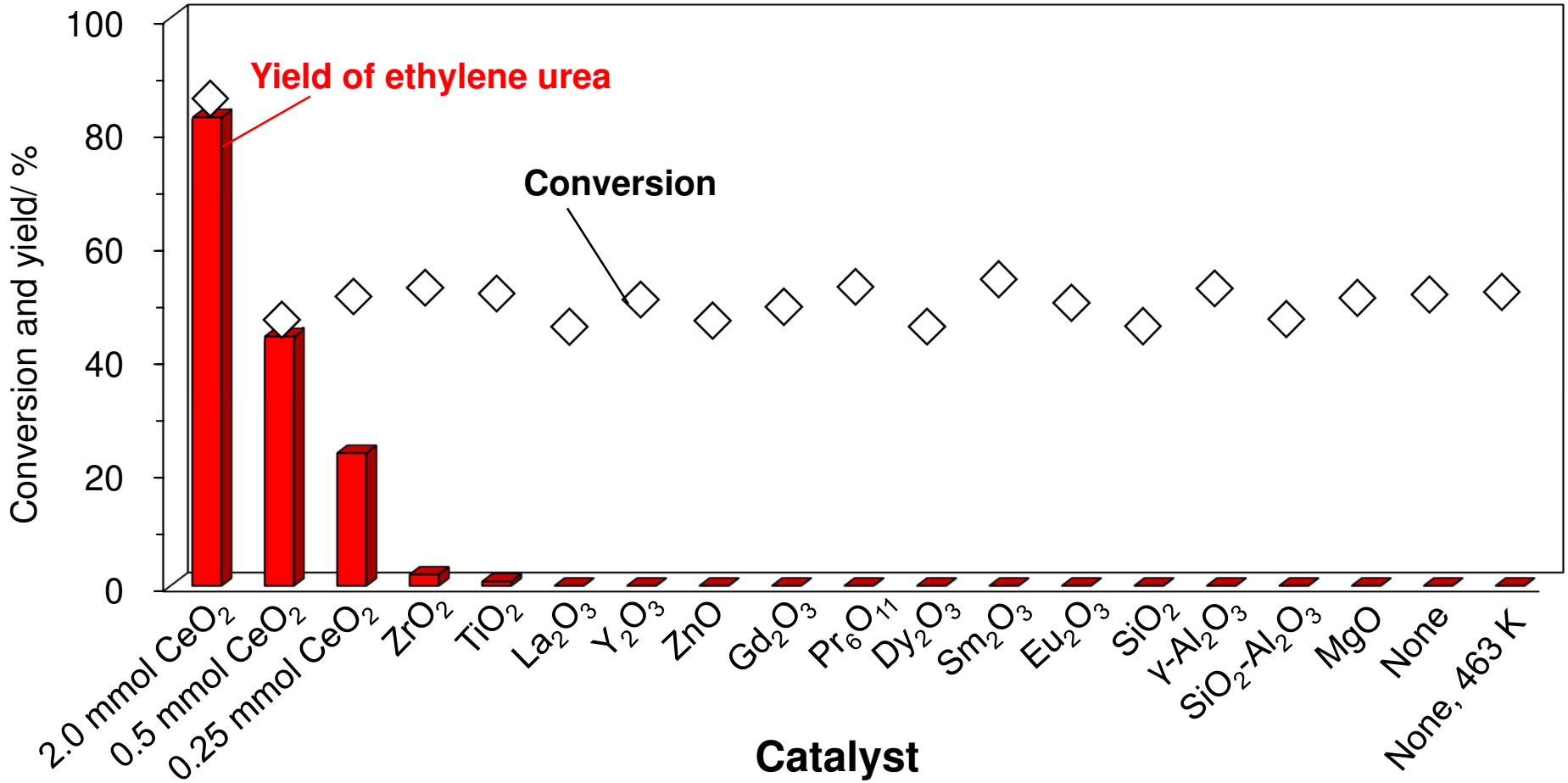

Reaction conditions: metal oxide 0.5 mmol (based on metal), EDA-CA 1.04 g (10 mmol), 2-propanol 10 ml, 413 K, 24 h, Ar 1 MPa (r.t.).

In the synthesis of ethylene urea from ethylenediamine carbamate, cerium oxide (CeO_2) acted as the most effective metal oxide catalyst.

Reusability test of CeO_2 catalyst

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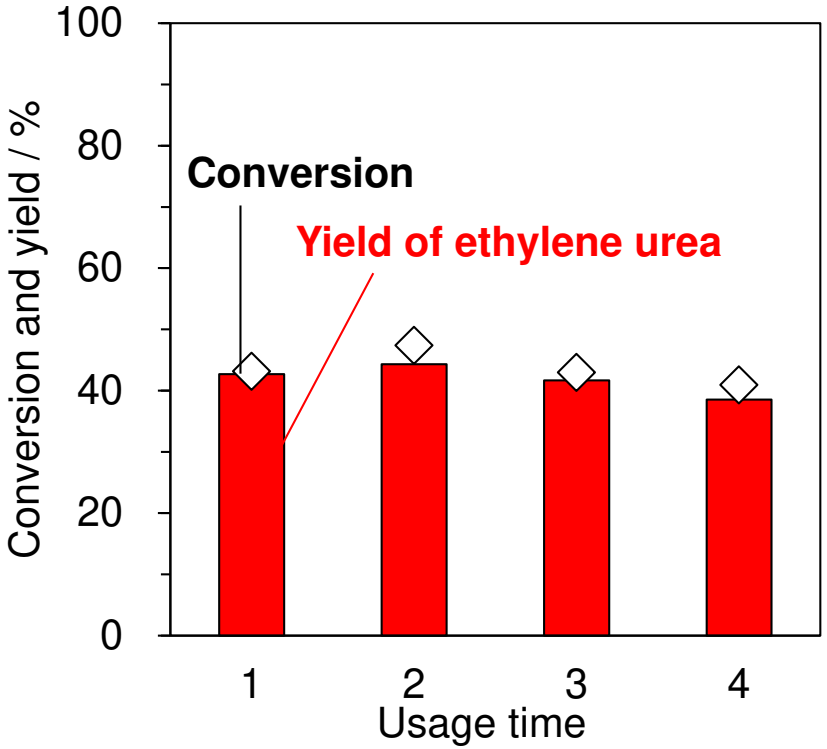
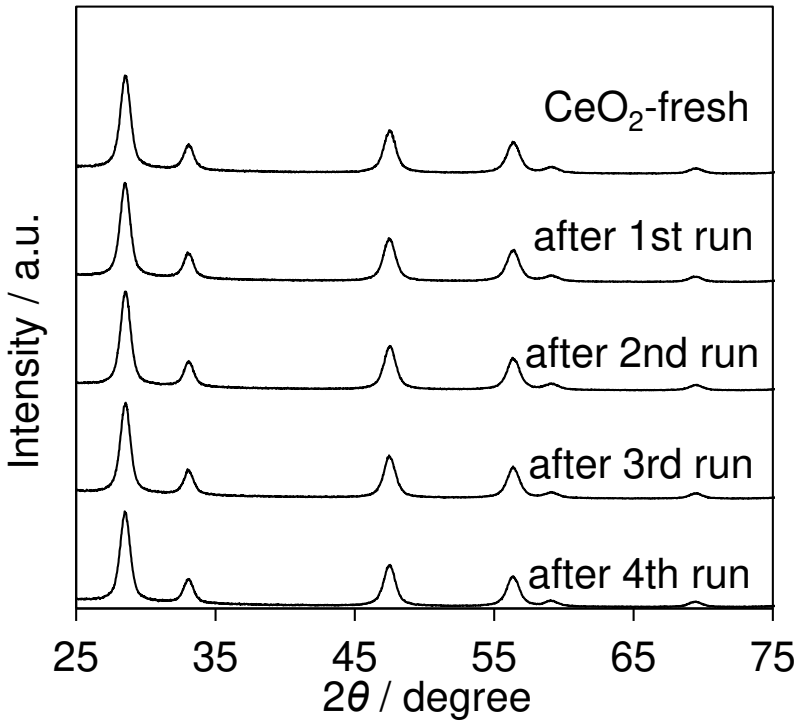
Method for catalyst reusability test

After the reaction, the catalyst is collected by filtration. → Catalyst washing → Catalyst drying (383 K, 3 h) → Reuse test

Conversion and yield



Catalyst characterization～XRD analyses～



	S_{BET} / $m^2 \cdot g^{-1}$	Particle size / nm
CeO_2-fresh	83	9
after 1st run	79	9
after 2nd run	78	9
after 3rd run	77	9
after 4th run	77	9

Reaction conditions: CeO_2 0.34g (2.0 mmol), EDA-CA 2.08 g (20 mmol), 2-propanol 15 ml, 413 K, 8 h, Ar 1 MPa (r.t.).

The cerium oxide catalyst can be reused without loss of activity or yield. The catalyst structure was not changed even after reuse, and therefore CeO_2 has high durability and reusability.

Proposed reaction mechanism

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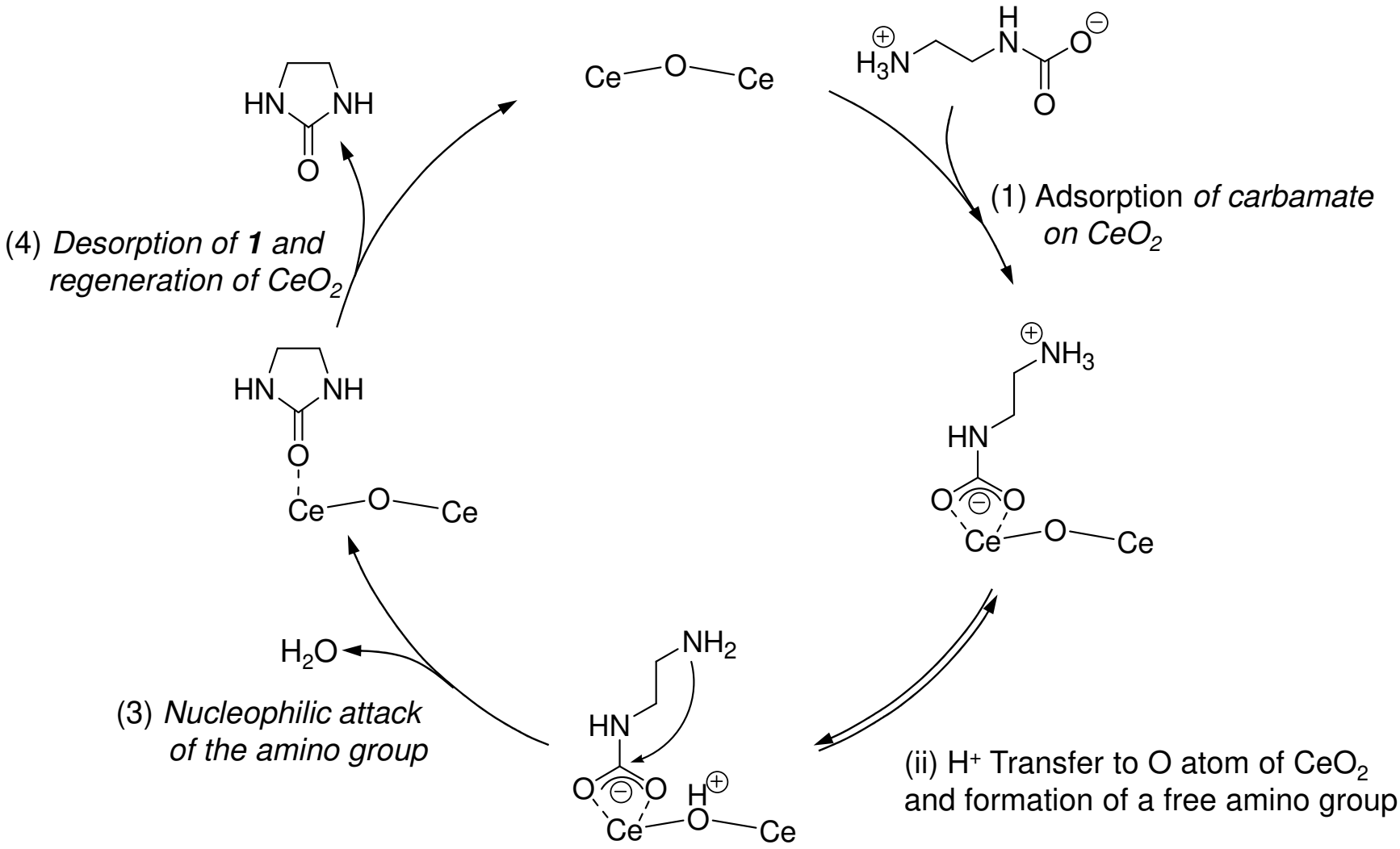
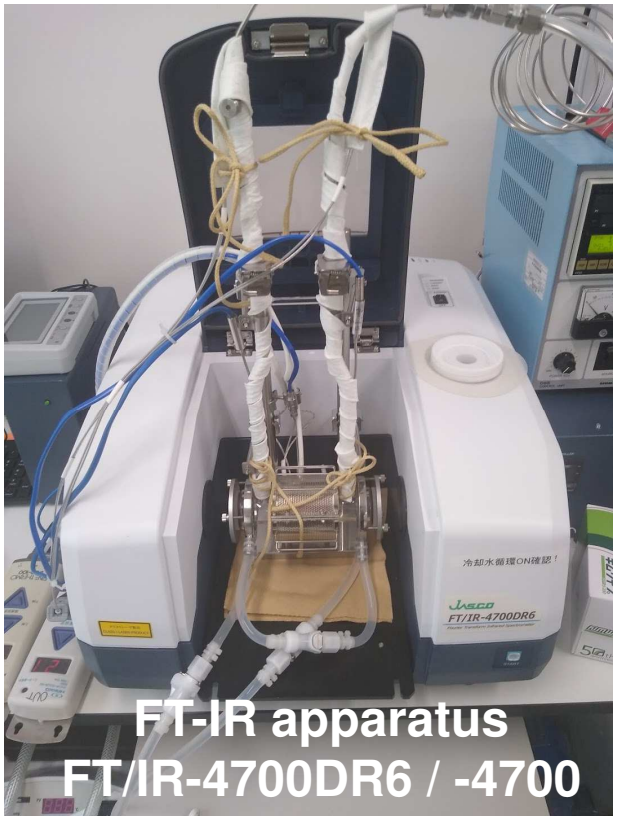
Proposed reaction mechanism for the synthesis of ethylene urea over cerium oxide catalyst



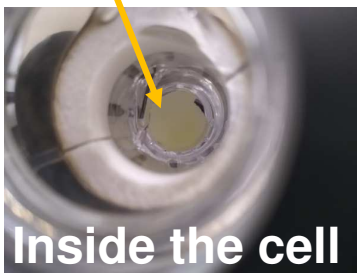
The acid-base bifunctionality of cerium oxide will contribute to the improvement of the reactivity of ethylenediamine carbamate.

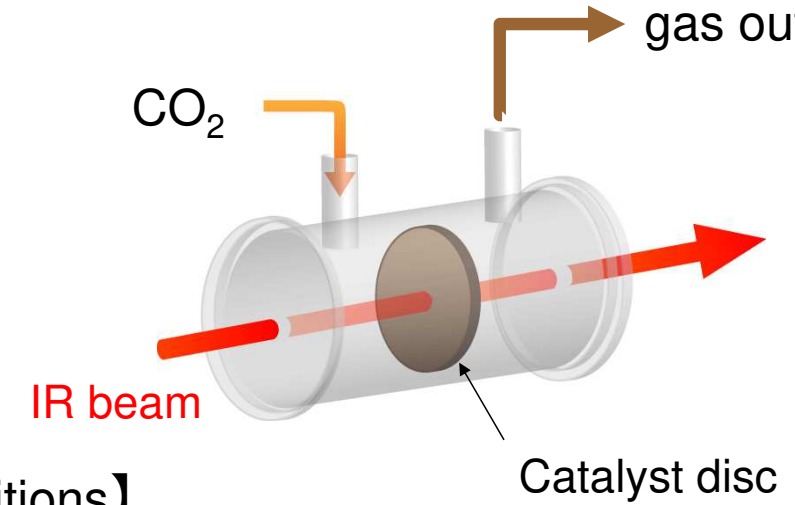
Analysis of adsorption behavior of CO_2 in air by FTIR

In situ FTIR apparatus (transmission measurement))



In situ FTIR image





【Measurement conditions】
Transmission, TGS detector

Method for CO_2 adsorption by FTIR

【CeO_2 pellet】
873 K calcined CeO_2
(60 ± 3 mg)

→ Pretreatment: He 30 mL/min, O_2 7.5mL/min, Lamp time 1 h, 873 K, 10 min

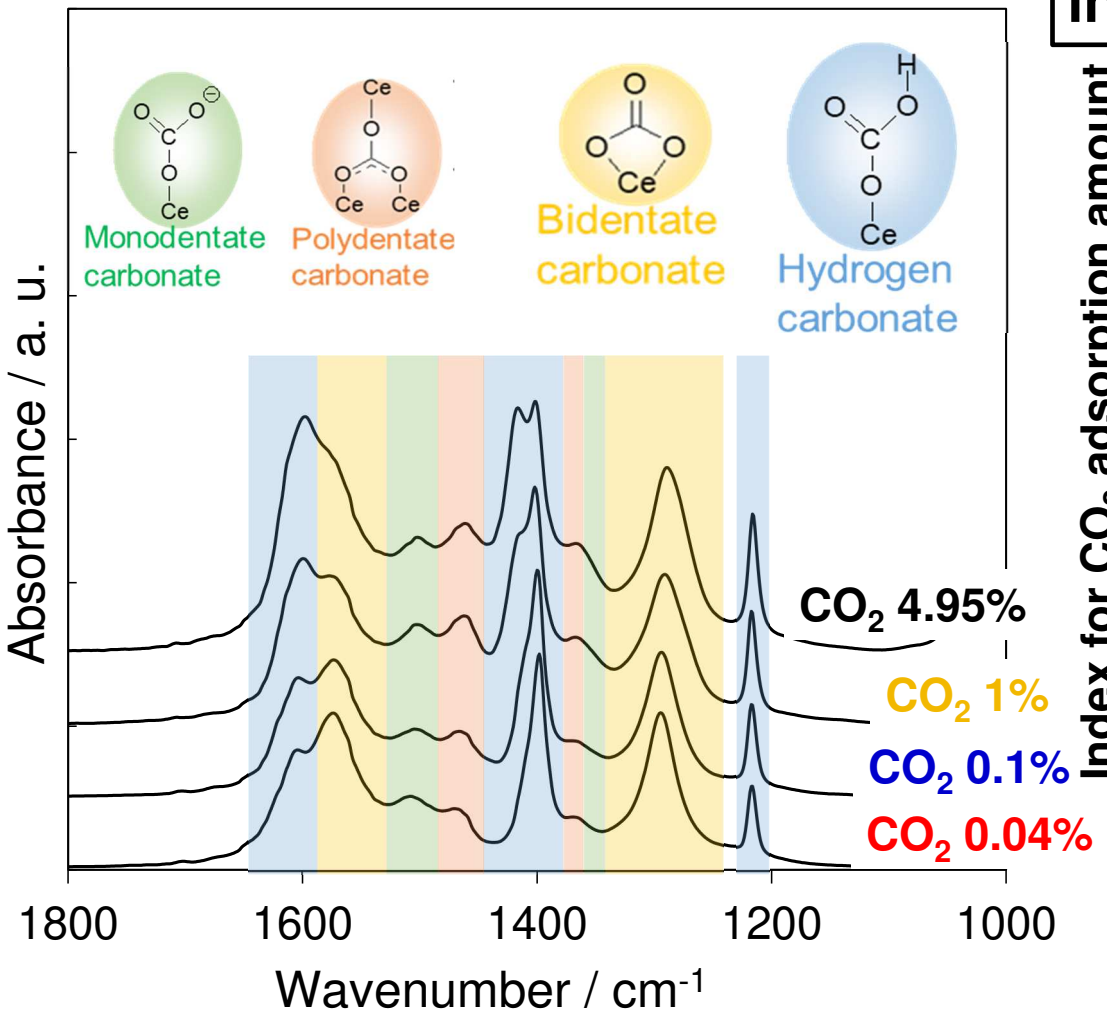
→ He flow (30 mL/min)

→ CO_2 introduction: 0.04~4.95 % CO_2/He 30 mL/min, 298 K

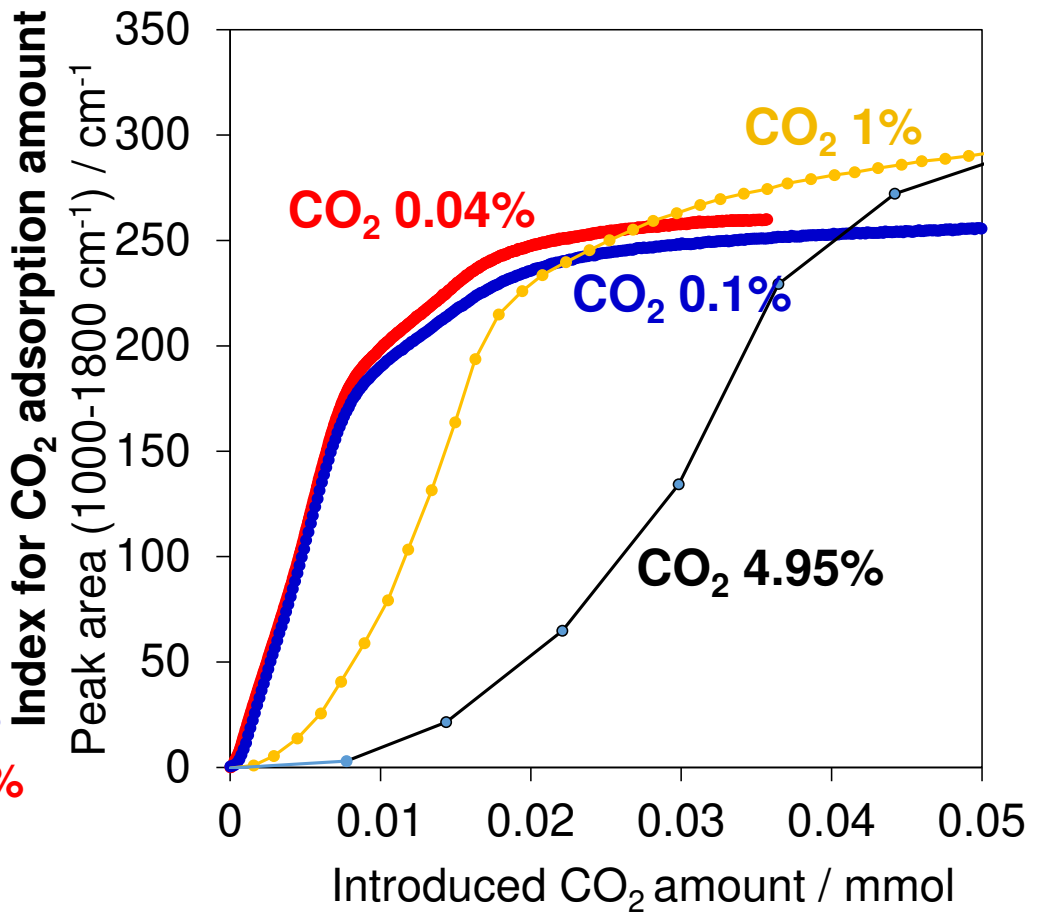
Various contents of carbon dioxide (0.04, 0.1, 1, 4.95%) were introduced to analyze the carbon dioxide adsorption behavior over cerium oxide.

Analysis of adsorption behavior of CO_2 in air by FTIR

FTIR spectra of carbon dioxide adspecies on cerium oxide.



Change in the adsorption amount of CO_2 as a function of the amount of introduced carbon dioxide



Even low-concentration carbon dioxide could be adsorbed on CeO_2 as efficient as or more efficient than high-concentration carbon dioxide.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