

CeO₂-Catalyzed Synthesis of 2-Imidazolidinone from Ethylenediamine Carbamate

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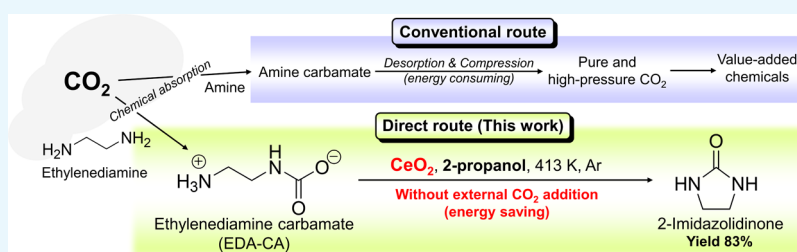
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ABSTRACT: CeO₂ acted as an effective and reusable heterogeneous catalyst for the direct synthesis of 2-imidazolidinone from ethylenediamine carbamate (EDA-CA) without further addition of CO₂ in the reaction system. 2-Propanol was the best solvent among the solvents tested from the viewpoint of selectivity to 2-imidazolidinone, and the use of an adequate amount of 2-propanol provided high conversion and selectivity for the reaction. This positive effect of 2-propanol on the catalytic reaction can be explained by the solubility of EDA-CA in 2-propanol under the reaction conditions and no formation of solvent-derived byproducts. This catalytic system using the combination of the CeO₂ catalyst and the 2-propanol solvent provided 2-imidazolidinone in up to 83% yield on the EDA-CA basis at 413 K under Ar. The reaction conducted under Ar showed a higher reaction rate than that with pressured CO₂, which clearly demonstrated the advantage of the catalytic system operated at low CO₂ pressure or even without CO₂.

INTRODUCTION

Cyclic ureas are important intermediates for pharmaceuticals, agricultural chemicals, natural products, chiral auxiliaries, and so on.¹ 2-Imidazolidinone is the simplest cyclic urea, and the synthesis from ethylenediamine (EDA) is often used as a model reaction for cyclic urea syntheses. The methods for the synthesis of 2-imidazolidinone are shown in Scheme 1. 2-Imidazolidinone is conventionally synthesized from EDA and hazardous carbonylation agents such as phosgene² and CO,³ and the stoichiometric amount of salts is produced by neutralization. Acyclic ureas⁴ and organic carbonates,⁵ both of which are typically synthesized with phosgene or CO as the carbonyl source, are also used as alternative carbonyl agents. The direct synthesis of 2-imidazolidinone from CO₂ and EDA is one of the promising and environmentally benign methods because the byproduct is only water, and various methods have been reported such as non-catalytic systems^{6–8} and catalytic systems including homogeneous catalyst systems,^{9–11} modified ionic liquids,^{12–14} and heterogeneous catalyst systems.^{15–19} However, in these reaction systems, pure and high-pressure CO₂ is required for obtaining the high yield of the target product based on EDA, which means that additional processes, equipment, and energy costs such as CO₂ desorption, purification, and compression are necessary.^{20,21} Therefore,

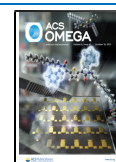
the direct transformation of captured CO₂ is a simple and desirable process.

CO₂ chemical absorption with amines is a useful and commercialized method,^{22–25} and the direct synthesis of ureas from CO₂ captured by amines (namely, amine carbamate) without desorption, purification, and compression is promising. Some researchers reported on the transformation of amine carbamates into organic ureas.^{26–29} Barzagli and co-workers reported that the CuCl₂ catalyst was effective for the synthesis of urea from ammonium carbamate with a yield of 54% (413 K, 3 days)²⁶ and 1,3-dialkyl ureas from the corresponding carbamates with a yield of 37–44% (423 K, 5 h).²⁷ Recently, Manaka and co-workers found that 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), an organic strong base, worked as an effective catalyst for the synthesis of urea from ammonium salts including ammonium carbamate, ammonium bicarbonate, and ammonium carbonate, and 35% yield of urea was obtained

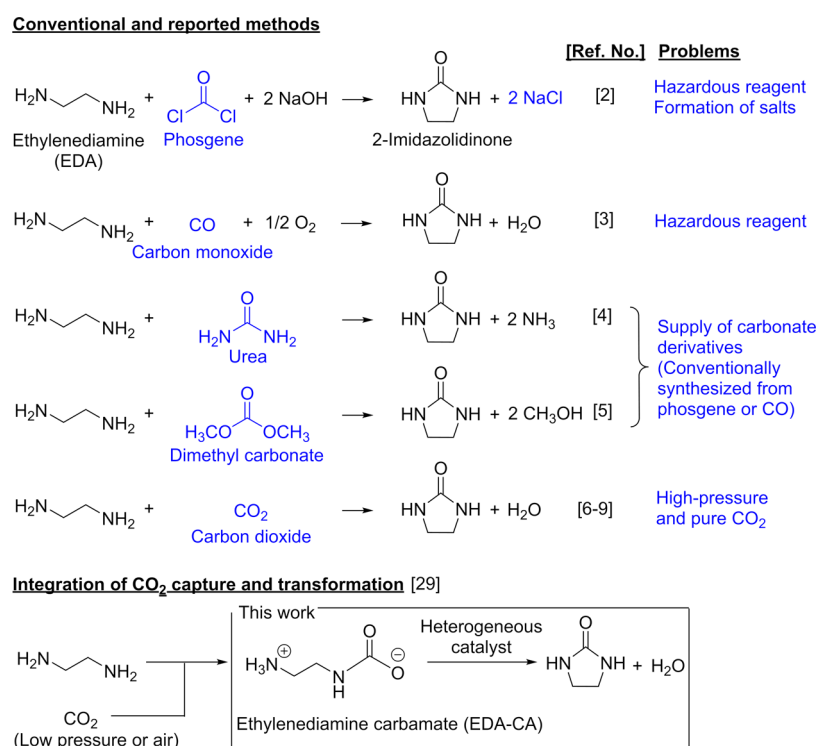
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Scheme 1. Various Methods for the Synthesis of 2-Imidazolidinone from EDA and This Work



from the ammonium salts in dimethyl sulfoxide at 373 K for 3 days.²⁸ However, these catalyst systems suffered from the low yields (<60%). Very recently, Choi and co-workers reported an effective homogeneous catalyst of Cp₂Ti(OTf)₂ for the synthesis of ureas including cyclic ureas from amine carbamates which were prepared from CO₂ and amines, and high yields of the target ureas (70–99%) were obtained.²⁹ However, these catalyst systems used homogeneous catalysts, and heterogeneous catalysts are preferable to homogeneous ones from the viewpoints of the durability, reusability, and ease of separation of catalysts from reaction mixtures. Hence, the development of effective heterogeneous catalysts for the synthesis of organic ureas from the corresponding carbamates is highly desirable. In the previous reports, CeO₂ is one of the effective heterogeneous catalysts for organic urea synthesis from amines with pure and pressurized CO₂^{15,17,30} as well as for the synthesis of organic carbonates³¹ from alcohols and CO₂ and organic carbamates^{32,33} from amines, alcohols, and CO₂. Therefore, CeO₂ is a promising candidate of the heterogeneous catalysts for the conversion of amine carbamates to the corresponding ureas.

Herein, we aimed to develop effective systems using heterogeneous catalysts for the synthesis of 2-imidazolidinone from ethylendiamine carbamate (EDA-CA) (Scheme 1). We found that CeO₂ was an effective heterogeneous catalyst for the reaction under Ar with an appropriate amount of the 2-propanol solvent, providing a high 2-imidazolidinone yield of 83% and high utilization of captured CO₂ in EDA-CA.

RESULTS AND DISCUSSION

At first, the catalytic performance of metal oxides in the synthesis of 2-imidazolidinone (1) from EDA-CA at 413 K under Ar was investigated (Table 1). Without any catalysts (entries 19 and 20), the conversion of EDA-CA was 51%; however, no formation of 1 was observed even at 463 K (entry

Table 1. Synthesis of 2-Imidazolidinone (1) from EDA-CA with Various Metal Oxides under Ar^a

$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NHCO}_2^- \xrightarrow[\text{Ar}]{\text{Metal oxide, 2-PrOH}} \text{HN(CH}_2\text{CH}_2\text{NH)}_2 + \text{H}_2\text{O}$

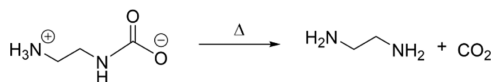
Ethylendiamine carbamate (EDA-CA) 2-Imidazolidinone (1)

entry	metal oxide	S ^b /m ² ·g ⁻¹	t/h	conv. ^c /%	selectivity ^c /%		yield ^c /%
					1	EDA	
1	CeO ₂	84	1	30	27	73	8
2	CeO ₂	84	24	46	96	4	44
3	ZrO ₂	44	24	52	4	96	2
4	TiO ₂	44	24	51	1	99	1
5	La ₂ O ₃	107	24	45	<1	>99	<1
6	Y ₂ O ₃	40	24	50	<1	>99	<1
7	ZnO	12	24	46	<1	>99	<1
8	Gd ₂ O ₃	60	24	49	<1	>99	<1
9	Pr ₆ O ₁₁	105	24	47	<1	>99	<1
10	Dy ₂ O ₃	58	24	45	<1	>99	<1
11	Sm ₂ O ₃	79	24	50	<1	>99	<1
12	Eu ₂ O ₃	69	24	49	<1	>99	<1
13	SiO ₂	453	24	45	<1	>99	<1
14	γ-Al ₂ O ₃	86	24	52	<1	>99	<1
15	SiO ₂ -Al ₂ O ₃	360	24	47	<1	>99	<1
16	MgO	31	24	50	<1	>99	<1
17	K ₂ CO ₃		24	53	<1	>99	<1
18	Cs ₂ CO ₃		24	52	<1	>99	<1
19	none		24	51	<1	>99	<1
20	none ^d		24	51	<1	>99	<1

^aReaction conditions: metal oxide 0.5 mmol (based on the metal), EDA-CA 1.04 g (9.8 mmol), 2-propanol 10 mL, 413 K. ^bSpecific surface area. ^cBased on EDA-CA. ^d463 K, Ar 1 MPa (r.t.).

20), which suggests that about half of EDA-CA was decomposed to EDA and CO₂ by heating in the absence of catalysts (Scheme 2). La₂O₃, Y₂O₃, ZnO, Gd₂O₃, Pr₆O₁₁,

Scheme 2. Decomposition of EDA-CA to EDA and CO₂



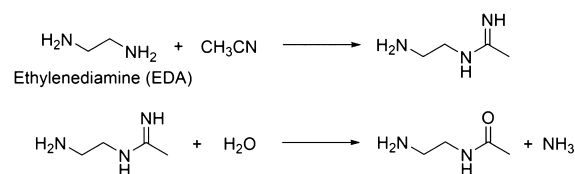
Dy₂O₃, Sm₂O₃, Eu₂O₃, SiO₂, γ -Al₂O₃, SiO₂-Al₂O₃, MgO, K₂CO₃, and Cs₂CO₃ (entries 5–18) showed almost no formation of **1** with about 50% conversion of EDA-CA, and EDA was formed as the main product by the decomposition of EDA-CA. On the other hand, CeO₂, ZrO₂, and TiO₂ showed activity in the reaction (entries 1–4). ZrO₂ and TiO₂ provided low **1** yields of 2 and 1%, respectively (entries 3 and 4); in contrast, CeO₂ gave high **1** yields of 8% at 1 h and 44% at 24 h (entries 1 and 2). Therefore, CeO₂ has high activity for the formation of **1** from EDA-CA compared with the decomposition of EDA-CA, leading to higher selectivity to **1** than the other metal oxides. CeO₂ is the most effective catalyst for the formation of **1**.

CeO₂ samples calcined at different temperatures were also applied to the same reaction (Figure S3 and Table S1). The conversion (24 h) showed a volcano-type tendency with respect to the calcination temperature, and CeO₂ calcined at 873 K provided the highest yield of **1**. This conversion behavior toward the calcination temperature is similar to that of our previous reports on CeO₂-catalyzed non-reductive transformation of CO₂ into organic carbonates^{34–42} and carbamates.^{32,43} This volcano-type relationship can be explained by the crystallinity and surface area of the catalysts. At a low calcination temperature of 673 K, the surface area of CeO₂ is high (~140 m² g⁻¹), but the crystallinity of CeO₂ is relatively low, that is, an amorphous phase is included, while the crystallinity of CeO₂ catalysts calcined at higher temperatures than 873 K is high (see Figure S4). The amorphous phase of CeO₂ calcined at 673 K will provide a negative effect on catalytic performance, leading to the low

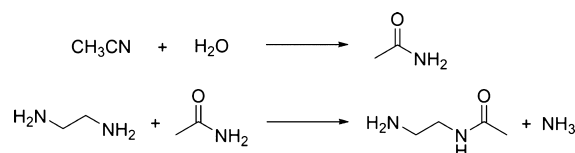
activity. On the other hand, a higher calcination temperature decreased the surface area, resulting in a decrease in active site amount and activity. Therefore, the intermediate calcination temperature of 873 K provided the most active CeO₂ catalyst. In the following studies, CeO₂ calcined at 873 K was used as the standard catalyst.

The effect of solvents was studied with methanol, ethanol, 1-propanol, 2-propanol, *tert*-butanol, CH₃CN, *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), and H₂O (Table 2). The yields of **1** in NMP (58%, entry 7) and THF (35%, entry 8) were much lower than those in the other solvents such as alcohols and CH₃CN (over 67%, entries 1–6). CH₃CN provided about 1 mmol solvent-derived products of *N*-(2-aminoethyl)acetamide and *N,N'*-diacetythylenediamine. These byproducts were formed *via* the reaction between EDA and CH₃CN (Scheme 3) or EDA and acetamide, which

Scheme 3. Formation of *N*-(2-Aminoethyl)acetamide *via* the Reaction of EDA and CH₃CN



Scheme 4. Formation of *N*-(2-Aminoethyl)acetamide *via* the Reaction of EDA and Acetamide



was formed by hydration of CH₃CN (Scheme 4) because the hydration of CH₃CN can be catalyzed by CeO₂.^{37,44,45} In the

Table 2. Effect of Solvents on the Synthesis of 2-Imidazolidinone (**1**) from EDA-CA^a

Entry	Solvent	Conv. ^b / %	Selectivity ^b / %			Yield ^b / %	Details of others / mmol
			1	EDA	Others		
1	Methanol	95	85	14	1	81	0.17
2	Ethanol	84	>99	<1	<1	84	0.07
3	1-Propanol	82	>99	<1	<1	82	0.07
4	2-Propanol	83	>99	<1	<1	83	Trace
5	<i>tert</i> -Butanol	67	>99	<1	<1	67	Trace
6	CH ₃ CN	82	96	<1	4	79	0.88 0.06
7	NMP	62	94	6	<1	58	0.01
8	THF	35	>99	<1	<1	35	Trace
9	H ₂ O	-	-	-	-	4	Trace

^aReaction conditions: CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), solvent 15 mL, 413 K, 24 h, Ar 1 MPa (r.t.). ^bBased on EDA-CA.

cases of primary alcohols such as methanol, ethanol, and 1-propanol (entries 1–3), a small amount of byproducts were produced by *N*-alkylation of EDA with the alcohols. In contrast, the secondary alcohol of 2-propanol (entry 4) and the tertiary alcohol of *tert*-butanol (entry 5) provided no byproduct with **1** yields of 83% and 67%, respectively. The bulkiness around the OH group suppressed the *N*-alkylation of EDA, leading to no production of byproducts. With the H₂O solvent (entry 9), the yield of **1** was only 4%. Even though EDA-CA can be dissolved in H₂O easily, the formation of **1** was suppressed by the presence of H₂O due to the equilibrium. Therefore, in terms of yield and selectivity, 2-propanol was selected as a suitable solvent for the reaction.

The effect of the 2-propanol solvent amount was then studied in the range between 1 and 30 mL (standard volume: 15 mL), and the conversion and yield at 24 h are shown in Figure 1 (details are shown in Table S2). The conversion and

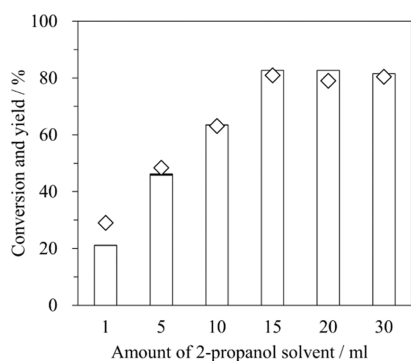


Figure 1. Effect of 2-propanol solvent amount on the synthesis of 2-imidazolidinone (**1**) from EDA-CA over CeO₂ [diamonds: conversion, white bars: yield of **1**, black bars: yield of *N,N'*-bis(2-aminoethyl)urea]. Reaction conditions: CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), 2-propanol, 413 K, 24 h, Ar 1 MPa (r.t.).

yield increased with the increase of the 2-propanol amount up to 15 mL, and they were constant with a higher amount of 2-propanol (about 80% conversion and yield). Focusing on the byproduct, the formation of *N,N'*-bis(2-aminoethyl)urea, a linear urea byproduct, was observed with less than 10 mL of 2-propanol. The conversion with **1** and 5 mL of 2-propanol is larger than the yield, and the difference between conversion and yield increased with the decrease of the 2-propanol amount due to the decomposition of a part of EDA-CA to EDA and CO₂ (Table S2 and Scheme 2), which suggests that the 2-propanol solvent can play a role in the suppression of the decomposition of EDA-CA. These results indicate that with a small amount of the 2-propanol solvent (0–10 mL) (Figure 1), EDA produced by decomposition of EDA-CA will react with **1**, providing *N,N'*-bis(2-aminoethyl)urea (Scheme 5), and the low reactivity will be related to the presence of EDA or CO₂ produced by decomposition of EDA-CA. To examine the reactivity of **1** with EDA, the reaction of **1** and EDA was

Scheme 5. Formation of *N,N'*-bis(2-Aminoethyl)urea from 2-Imidazolidinone (1**) and EDA**



conducted in the presence or absence of the CeO₂ catalyst (Table S3). The formation of *N,N'*-bis(2-aminoethyl)urea was confirmed in both cases, and the reaction can proceed without CeO₂. The formation of *N,N'*-bis(2-aminoethyl)urea was also supported in terms of the formation energy, which was estimated by DFT calculations (Table S4). The formation of *N,N'*-bis(2-aminoethyl)urea from **1** and EDA can be exothermic (−31 kJ mol^{−1}, entry 5, Table S4), whose energy change is larger than the case of the formation of *N,N'*-bis(2-aminoethyl)urea from CO₂ and EDA (−19 kJ mol^{−1}, entry 4, Table S4). Therefore, the formation of *N,N'*-bis(2-aminoethyl)urea from **1** and EDA is easier than that from CO₂ and EDA, and the EDA formed by the decomposition of EDA-CA in the case of a small amount of the 2-propanol solvent can react with **1** to provide the linear urea of *N,N'*-bis(2-aminoethyl)urea. As above, the proper amount of the 2-propanol solvent (≥15 mL) is required for the high conversion and selectivity.

The reaction temperature dependence was examined in the range between 373 and 453 K. The time courses at each temperature are shown in Figure 2 (the detailed data are in Table S5). The yield of **1** increased smoothly with the reaction time at any reaction temperatures and reached the equilibrium in 72 h at higher reaction temperatures than 403 K. Focusing on the equilibrium yields (Figure 2d–f), the yield of **1** decreased from 83 to 70% with the increase of the reaction

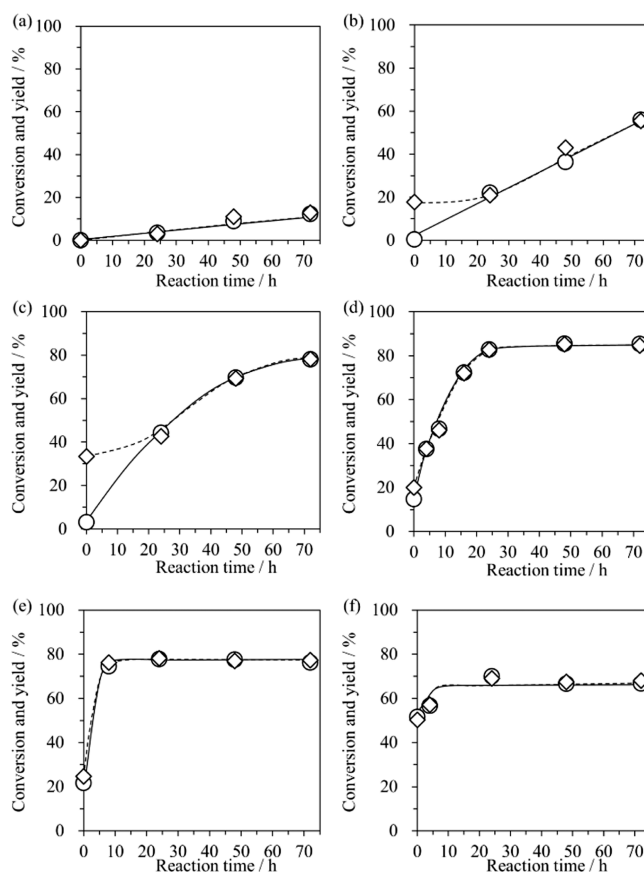


Figure 2. Time courses of the synthesis of 2-imidazolidinone (**1**) from EDA-CA over CeO₂ at (a) 373 K, (b) 393 K, (c) 403 K, (d) 413 K, (e) 433 K, and (f) 453 K (diamonds: conversion, circles: yield). Reaction conditions: CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), 2-propanol 15 mL, Ar 1 MPa (r.t.).

temperature. Based on the DFT calculations (Table S4), the formation of **1** from EDA-CA is an endothermic reaction (+27 kJ mol⁻¹, entry 3, Table S4). Therefore, the higher equilibrium yield at a lower reaction temperature is probably due to the entropic effect of the reaction because the 2 moles of molecules, **1** and water, are formed from the 1 mole of EDA-CA molecules. The highest yield of 83% was obtained at 413 K with a proper amount of the 2-propanol solvent (15 mL). The formation rate was calculated from the slope of the time course at a low conversion level (<40%, Figure S5 and Table S6) to be 0.60 h⁻¹ at 413 K. The value is a little higher than that with the reported homogeneous catalyst system of Cp₂Ti(OTf)₂ (0.47 h⁻¹) at 433 K²⁹ despite the 20 K lower reaction temperature. Koizumi and co-workers reported that CeO₂ (<25 nm) was active for the synthesis of **1** from EDA-CA, but the activity was low (yield 29%, 443 K).²⁹ In contrast, in our case, by using nano-CeO₂ (84 m²/g, 9 nm), the yield reached 83% at a low temperature of 413 K, and such a lower reaction temperature is beneficial for the suppression of EDA-CA decomposition. These results mean that our CeO₂ catalyst is quite active for the reaction. In terms of the activity and equilibrium yield, 413 K was used in the following studies.

The effect of CO₂ addition on the synthesis of **1** from EDA-CA was investigated (Figure 3 and the detailed data are in

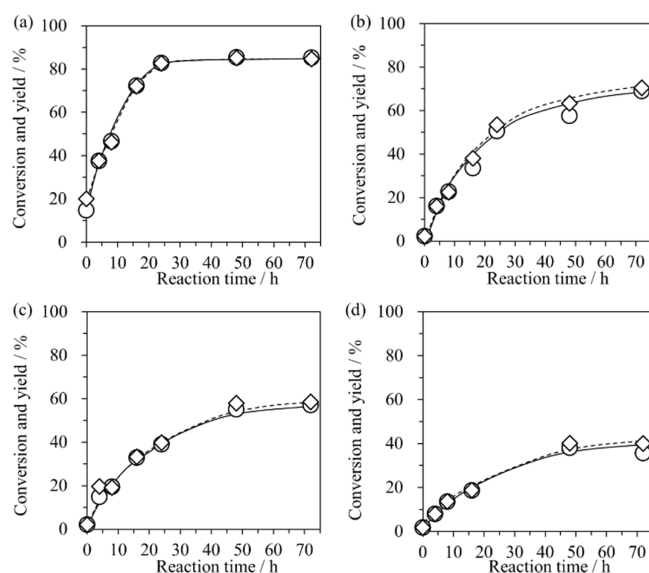


Figure 3. Effect of external CO₂ addition on the synthesis of 2-imidazolidinone (**1**) from EDA-CA over CeO₂ (diamonds: conversion, circles: yield). Reaction conditions: CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), 2-propanol 15 mL, (a) 1 MPa Ar (r.t.), (b) 0.5 MPa CO₂ (r.t.) (ca. 40 mmol), (c) 1 MPa CO₂ (r.t.) (ca. 80 mmol), and (d) 2 MPa CO₂ (r.t.) (ca. 175 mmol).

Table S7). The reaction rate clearly decreased with the increase of the CO₂ pressure. Therefore, CO₂ gives a negative effect on the reaction rate, demonstrating that the catalytic system for converting EDA-CA to **1** without the further CO₂ addition is advantageous over the reactions operated with CO₂. This result supports that the lower reaction rate in the case of a smaller amount of the 2-propanol solvent (Figure 1) is caused by CO₂ produced *via* the decomposition of EDA-CA. The negative effect of the presence of external CO₂ on the formation rate of 2-imidazolidinone from EDA-CA can be explained by the conversion of the reactive amino group of

EDA-CA adspecies with CO₂ to the corresponding carbamic acid with lower reactivity.

The reusability of the CeO₂ catalyst in the synthesis of **1** from EDA-CA was elucidated (Figure 4, the detailed data are

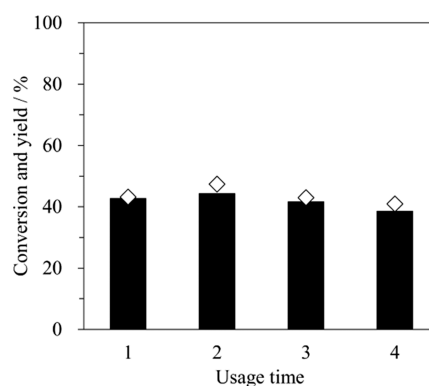


Figure 4. Reusability test of CeO₂ in the synthesis of 2-imidazolidinone (**1**) from EDA-CA (diamonds: conversion, black bars: yield of **1**). Reaction conditions: CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), 2-propanol 15 mL, 413 K, 8 h, Ar 1 MPa (r.t.).

summarized in Table S8). After each reaction, the spent CeO₂ catalyst was dried at 383 K for 3 h for the next run. In the reuse test, the yield was not changed at least three times. The X-ray diffraction (XRD) patterns of CeO₂ catalysts before and after the reaction were not changed, and no decrease of the specific surface area was observed (Figure 5). These results indicate that CeO₂ is a reusable heterogeneous catalyst and robust against the reaction and regeneration treatment.

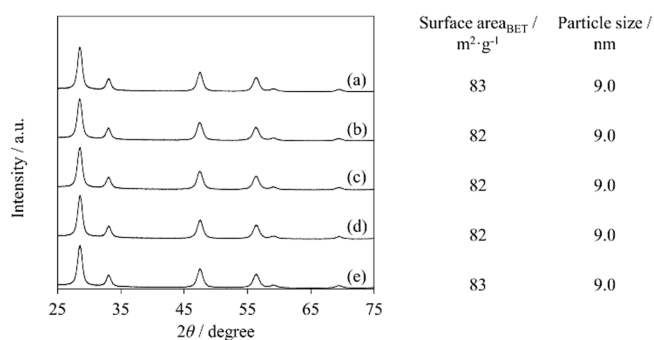


Figure 5. XRD patterns, specific surface area, and particle size of CeO₂ catalysts in the reusability test. (a) Fresh CeO₂, (b) CeO₂ after the first run, (c) CeO₂ after the second run, (d) CeO₂ after the third run, (e) and CeO₂ after the fourth run.

The pressure and temperature of the autoclave reactor during the heating and reaction were monitored with the following three cases (Figure 6): (i) 2-propanol + Ar, (ii) 2-propanol + EDA-CA + Ar, and (iii) 2-propanol + EDA-CA + CeO₂ + Ar. The pressure increased with the increase of the reaction temperature in all the cases. In case (i), the pressure reached about 1.8 MPa. Considering that the values of (vapor) pressure of 1 MPa Ar and 2-propanol are about 1.37 and 0.67 MPa at 413 K based on the ideal gas, respectively, the ideal total pressure of case (i) is about 2.0 MPa, which is similar to the observed one (1.8 MPa). On the other hand, in the cases with EDA-CA [cases (ii) and (iii) in Figure 6], the pressure reached about 2.0 MPa at 413 K, which is higher than that of

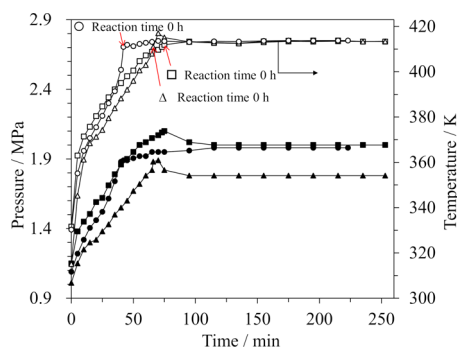


Figure 6. Behavior of pressure and temperature in the autoclave reactor. (i) 2-Propanol + Ar (pressure ▲, temperature Δ), (ii) 2-propanol + EDA-CA + Ar (pressure ■, temperature □), and (iii) 2-propanol + EDA-CA + CeO₂ + Ar (pressure ●, temperature ○). Conditions of (i) 2-propanol 15 mL, Ar 1 MPa (r.t.); (ii) EDA-CA 2.08 g (19.6 mmol), 2-propanol 15 mL, Ar 1 MPa (r.t.); (iii) CeO₂ 0.34 g (2.0 mmol), EDA-CA 2.08 g (19.6 mmol), 2-propanol 15 mL, Ar 1 MPa (r.t.).

case (i) (1.8 MPa). The difference in the pressures is about 0.2 MPa. The conversion (or decomposition) of EDA-CA was also determined by GC in the cases of (ii) and (iii) (Table S9). The decomposition in the case of (ii) was about 38%, and 7.5 mmol of CO₂ and 7.5 mmol of EDA were formed (entry 1 in Table S9). Considering the estimated (vapor) pressure of EDA at 413 K (~0.2 MPa)⁴⁶ and 7.5 mmol CO₂ (~0.14 MPa), the observed pressure difference (0.2 MPa) is lower than the total estimated (vapor) pressure of EDA and CO₂ (0.34 MPa) at 413 K, which will be due to the suppression of EDA-CA decomposition or the dissolution of EDA and CO₂ in the solvent. The pressure of actual reaction [case (iii) in Figure 6] was slightly lower than that without the CeO₂ catalyst [case (ii) in Figure 6], which may be due to the formation of **1** by CeO₂ in case (iii).

Moreover, to investigate the state of the reaction mixture during heating more intuitively, direct monitoring with a transparent glass tube was conducted with the same three cases above. The reactor volume was 10 mL, and the scale was reduced to one-fifth of that of the reaction conditions for the autoclave reactor employed above. The behavior of the pressure and temperature is shown in Figure S7, and the pictures of reaction media during heating are shown in Figure S8. In the direct monitoring, similar pressure changes and a similar pressure gap between cases (i) and (ii) to the cases of the autoclave reactor (Figure 6) were observed (0.1–0.2 MPa) (Figure S7). When the temperature reached 413 K (21 min), the pressures were almost the same in all the cases. Afterward, the pressure of cases (ii) and (iii) increased up to about 81 min and decreased gradually at a longer reaction time, while the pressure of case (i) was not changed. The pressure increases after 21 min in the cases of (ii) and (iii) can be attributed to the decomposition of EDA-CA to CO₂ and EDA. Focusing on the pictures of the reaction media (Figure S8), case (i) showed that the liquid was always transparent (Figure S8). In contrast, in the cases of (ii) and (iii) (Figure S8), EDA-CA was in the solid state up to 413 K (0–21 min) and subsequently started to be dissolved and completely dissolved at 81 min. The starting time of solid dissolution was the same as the time when the pressure gap between case (i) and cases (ii) and (iii) appeared, which supports that the pressure gap is due to the decomposition of EDA-CA to CO₂ and EDA. These results

also suggest that the 2-propanol solvent suppressed the decomposition of EDA-CA, which is related to the results of the solvent amount effect (Figure 1). Some white solids were formed on the wall of the top of the tube after 81 min in the cases of (ii) and (iii) (Figure S8). This is because CO₂ and EDA, which were produced by the decomposition of EDA-CA, reacted at the top of the reactor to form EDA-CA again on the wall of the test tube, leading to the decrease of the total pressure.

CONCLUSIONS

We found that CeO₂ was the most effective catalyst for the synthesis of 2-imidazolidinone from EDA-CA in the absence of external CO₂ among the various metal oxides tested. 2-Propanol was the best solvent by the suppression of the formation of solvent-derived products. The combination of the CeO₂ catalyst and an adequate amount of the 2-propanol solvent provided 2-imidazolidinone in high yield of 83% at 413 K, and CeO₂ was a reusable heterogeneous catalyst and robust against the reaction and recovery treatment. The investigation of the solvent amount effect of 2-propanol on the reaction of EDA-CA suggests that the formation of *N,N'*-bis(2-aminoethyl)urea is suppressed with the sufficient amount of the 2-propanol solvent, which can be interpreted by the suppression of decomposition of EDA-CA in the presence of the 2-propanol solvent. According to the direct monitoring of the reaction media and the measurement of the total pressure of the autoclave during the reaction, most EDA-CA can be solved in the 2-propanol solvent, suggesting that EDA-CA is directly converted to 2-imidazolidinone catalyzed by CeO₂. The negative effect of the external CO₂ on the reaction also demonstrates the superiority of the catalytic conversion of EDA-CA to 2-imidazolidinone over CeO₂ in the absence of external CO₂.

EXPERIMENTAL SECTION

Catalysts and Reagents. Metal oxides were commercially available and used as received or after calcination: CeO₂ (Daiichi Kigenso Kagaku Kogyo Co., Ltd., CeO₂-HS, calcined at 873 K in air for 3 h), ZrO₂ (Daiichi Kigenso Kagaku Kogyo Co., Ltd., RC-100 P, calcined at 873 K in air for 3 h), TiO₂ (Nippon Aerosil P25, calcined at 873 K in air for 3 h), La₂O₃ (Kanto Chemical Co., Inc., used as received), Y₂O₃ (Kanto Chemical Co., Inc., used as received), ZnO (Kanto Chemical Co., Inc., used as received), Gd₂O₃ (Kanto Chemical Co., Inc., used as received), Pr₆O₁₁ (Kanto Chemical Co., Inc., used as received), Dy₂O₃ (Kanto Chemical Co., Inc., used as received), Sm₂O₃ (Kanto Chemical Co., Inc., used as received), Eu₂O₃ (Kanto Chemical Co., Inc., used as received), SiO₂ (Fuji Silysia Chemical Ltd., G6, calcined at 773 K in air for 3 h), γ -Al₂O₃ (Nippon Aerosil, calcined at 873 K in air for 3 h), SiO₂-Al₂O₃ (Reference Catalyst Division of the Catalysis Society of Japan, JRC-SAL-2, a SiO₂/Al₂O₃ ratio of 5.5, used as received), and MgO (Ube Industries, Ltd., MgO 500A, calcined at 873 K in air for 3 h).

It was already reported that EDA-CA typically in an EDA/CO₂ = 1:1 complex can be obtained from EDA and low-pressure CO₂ of 0.1 or 0.01 MPa and even CO₂ (~0.04%) in air.^{29,47–50} The substrate of EDA-CA used in this work was synthesized in our laboratory. 20 g of EDA and 20 g of ethanol (solvent) were put into a 190 mL autoclave. The autoclave was purged with 1 MPa CO₂ twice and then was pressurized to 5

MPa by CO₂. The mixture in the autoclave was stirred at room temperature and 300 rpm for 20 h. Then, it was filtered, washed with ethanol, and dried at 333 K overnight. The obtained white solid (yield 41%) was characterized by GC, thermogravimetric analysis–differential thermal analysis (TG-DTA) (Figure S1), and CHNS elemental analysis [C: 34.71, H: 7.85, N: 27.16; ideal composition (C: 34.61, H: 7.74, N: 26.91, O: 30.74)]. The purity of EDA-CA in the obtained solid was 98%, and the impurity of EDA in the obtained solid was estimated to be 2% based on GC and CHNS elemental analysis results. Other chemicals were purchased from chemical companies and used without further purification.

Characterization of Catalysts. The specific surface areas of metal oxides were measured by the BET method (N₂ adsorption) with a Micromeritics Gemini VII 2360. The XRD patterns were obtained using a Rigaku MiniFlex600 diffractometer [Cu K α (λ = 0.154 nm), 40 kV, 20 mA] under air. The TG and DTA data were recorded using a Rigaku Thermo Plus EVOII instrument. The CHNS elemental analysis was carried out with an Elementar vario EL cube.

Typical Procedure for the Synthesis of 2-Imidazolidinone (1) from EDA-CA. The reactions were carried out in a 190 mL autoclave reactor. The typical procedure for the reaction was as follows: 0.34 g (2.0 mmol) of CeO₂, 15 mL of 2-propanol, and 2.08 g (19.6 mmol) of EDA-CA were put into the autoclave with a spinner. The autoclave was sealed, purged twice with 1 MPa Ar, and pressurized to 1 MPa by Ar at room temperature. The autoclave was heated to 413 K, and the time when the temperature just reached 413 K was defined as 0 h of reaction time. After the reaction, the autoclave was cooled down to room temperature in a water bath. EDA-CA decomposes into EDA and CO₂ in the injection chamber of the GC system due to high temperature, and hence, the direct analysis of EDA-CA is impossible. EDA-CA easily dissolves in H₂O but cannot dissolve in ethanol. In contrast, EDA can easily dissolve in ethanol. Based on the different dissolution properties of EDA and EDA-CA, the following collecting method was adopted, and the procedure is illustrated in Figure S2. The reaction mixture including CeO₂ and the white solid was collected with ethanol (25 g). The liquid phase (i.e., ethanol solution containing 2-imidazolidinone and EDA) and the solid phase containing CeO₂ and unreacted EDA-CA were separated by filtration. The filtrate was analyzed by FID-GC (Shimadzu) with a capillary column (InertCap for Amine column, 0.32 mm, 30 m) by using 1-hexanol as an internal standard. The collected solid phase containing CeO₂ and unreacted EDA-CA were washed with H₂O (30 g), and CeO₂ was separated by filtration. The filtrate was analyzed using the same GC system. The qualitative analysis of products was performed on GC–MS (EI and CI, InertCap for Amine capillary column).

The conversion of EDA-CA, yield of products based on EDA-CA, and balance based on EDA were calculated as follows:

$$\text{conversion} = \left[1 - \frac{n_{\text{EDA-CA}}^{\text{detected}}}{n_{\text{EDA-CA}}^{\text{introduced}}} \right] \times 100\%$$

$$\text{yield based on EDA-CA} = \frac{n_{\text{products}}}{n_{\text{EDA-CA}}^{\text{introduced}}} \times 100\%$$

$$\text{balance} = \frac{n_{\text{products}} + n_{\text{EDA-CA}}^{\text{detected}}}{n_{\text{EDA-CA}}^{\text{introduced}} + n_{\text{EDA imp}}^{\text{introduced}}} \times 100\%$$

where $n_{\text{EDA-CA}}^{\text{introduced}}$ is the amount of EDA-CA (in mmol) that was introduced into the reactor, $n_{\text{EDA-CA}}^{\text{detected}}$ is the amount of EDA-CA (in mmol) that was detected, n_{products} is the amount of products (in mmol), and $n_{\text{EDA imp}}^{\text{introduced}}$ is the amount of EDA impurity (in mmol) that was introduced into the reactor.

For the reactions performed in a CO₂ atmosphere, the yield of products was based on EDA and calculated as follows:

$$\text{yield based on EDA} = \frac{n_{\text{products}}}{n_{\text{EDA-CA}}^{\text{introduced}} + n_{\text{EDA imp}}^{\text{introduced}}} \times 100\%$$

Reusability Test. The reusability test of CeO₂ was conducted as follows: after the reaction, the used catalyst was dried at 383 K for 3 h. During the recovery procedure, about 10 wt % CeO₂ was lost; therefore, multiple batches were conducted at the same time under the same reaction conditions to collect an enough amount of the used catalyst for the next run (first run: 4 batches, second run: 3 batches, third run: 2 batches, and fourth run: 1 batch).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04516>.

Detailed data for the graph in the main text and characterization results including XRD, BET, TG-DTA, and NMR (PDF)

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Notes

The authors declare no competing financial interest.

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