



Organic carbonate synthesis from CO₂ and alcohol over CeO₂ with 2-cyanopyridine: Scope and mechanistic studies



Masayoshi Honda^a, Masazumi Tamura^a, Yoshinao Nakagawa^a, Kenji Nakao^b, Kimihito Suzuki^b, Keiichi Tomishige^{a,*}

^a Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai 980-8579, Japan

^b Advanced Technology Research Laboratories, Nippon Steel & Sumitomo Metal, 20-1, Shintomi, Futtsu, Chiba 293-8511, Japan

ARTICLE INFO

Article history:

Received 13 March 2014

Revised 20 June 2014

Accepted 27 July 2014

Keywords:

Cerium oxide

CO₂

Carboxylation

Hydration

Organic carbonate

ABSTRACT

The combination system of CeO₂-catalyzed carboxylation and 2-cyanopyridine hydration (CeO₂ + 2-cyanopyridine system) is effective for the direct synthesis of organic carbonates from CO₂ and alcohols. This catalyst system can be applied to various alcohols to afford the corresponding carbonates in high alcohol-based yields. The hydration of 2-cyanopyridine over CeO₂ rapidly proceeds under the low concentration of water, which can remove the water from the reaction media. Since the reaction is limited by the chemical equilibrium, the removal of water remarkably shifts the chemical equilibrium to the carbonate side, leading to high carbonate yields. In addition, 2-picolinamide that is produced by hydration of 2-cyanopyridine forms an intramolecular hydrogen bonding between H atom of the amide group and N atom of the pyridine ring, which weakens the adsorption of 2-picolinamide on CeO₂ by reduction of the acidity. The reaction mechanism of DMC formation in CeO₂ + 2-cyanopyridine system is also proposed.

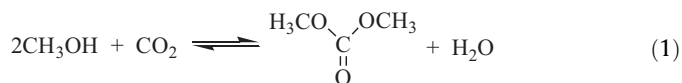
© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The direct synthesis of chemicals and fuels from CO₂ attracts more and more interest since CO₂ is an abundant, non-toxic and inexpensive carbon source [1]. Many attempts have been made for the reduction of CO₂ such as the conversion to formic acid [2] and methanol [3], however, the reductive transformation of CO₂ generally requires a large energy input since CO₂ is the most oxidized compound of carbon [1a]. On the other hand, non-reductive transformation of CO₂ to carbonate [4] and carbamate [5] is attractive since these reactions are energetically-favorable and as a result require less energy input. In particular, organic carbonates are plausible synthetic targets from the viewpoint of green sustainable chemistry for their low toxicity, non-corrosivity and biodegradability [6]. In addition, carbonates have been widely used as starting materials of polycarbonate resins [7], electrolytes of lithium ion battery [8], alkylating and carbonylating reagents [9], and inert solvents [6a]. Moreover, they are expected to be fuel additives in the future [10].

Organic carbonates have been traditionally produced by using phosgene or its derivatives [11]. However, this production process has considerable drawbacks such as use of highly toxic phosgene

and co-production of large amount of salts by the neutralization. Some alternative routes have been developed such as oxidative carbonylation of alcohols [12], alcoholysis of ureas, [13] and transesterification of dimethyl carbonate (DMC) with alcohols [14]. The reactions using organic reagents such as alkyl halides [15] and the electrochemical methodology have been also reported [16]. In contrast, catalytic process to directly synthesize organic carbonates from CO₂ and alcohols will be a promising methodology since water is the sole by-product and CO₂ is used as the carbon resource. In addition, some alcohols can be derived from biomass in the biorefinery [17]. For example, ethanol can be produced by the fermentation of starch or cellulose [18]. 1-Propanol can be also prepared by the hydrogenolysis of glycerol that is a major by-product in the biodiesel production from vegetable oils [19]. A typical target of organic carbonate synthesis is DMC from CO₂ and methanol (Eq. (1)).

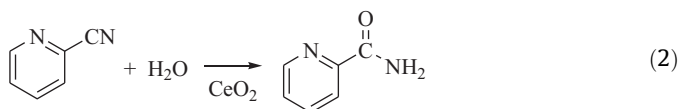


Various homogeneous [20] and heterogeneous [21] catalysts have been developed for this reaction, and our group has reported that ZrO₂ [22a,22b], H₃PO₄/ZrO₂ [22c,22d], CeO₂-ZrO₂ solid solutions [22e,22f], and CeO₂ [22g] work as heterogeneous catalysts. However, DMC yield based on methanol is low (e.g., DMC yield

* Corresponding author. Fax: +81 22 795 7214.

E-mail address: tomi@erec.che.tohoku.ac.jp (K. Tomishige).

2.1% under the conditions of dibutyltin dimethoxide catalyst, CO₂ 300 atm, 453 K, 24 h [1d]) and far from satisfactory due to the equilibrium limitation of Eq. (1) [20–23]. In order to improve the low DMC yield, several attempts have been made for removal of co-produced water from the reaction media, shifting the chemical equilibrium to the carbonate side [20a–f, 21a–c, 24, 25]. In particular, it has been reported that effective dehydrating reagents for removal of water were acetal, carbodiimide and epoxide, affording high yields based on the dehydrating reagents. For examples, Bu₂Sn(OMe)₂/2,2-dimethoxy propane (DMP) [26], CuCl/dicyclohexyl carbodiimide (DCC), [20d] and ZrO₂-KCl-Mg/butylene oxide [21a] systems provided 88%, 83%, and 49% DMC yields based on the dehydrating reagents, respectively. However, DMC yields based on methanol were very low (2%, 6%, 7%, respectively). From the viewpoint of DMC purification, complete conversion of methanol, that means high methanol-based DMC yields, is highly desirable since methanol and DMC form an azeotrope [27]. However, DMC yields based on methanol in the literatures were below 50% so far [1b]. Recently, we have found that the combination of CeO₂-catalyzed carboxylation of methanol and CO₂ and hydration of 2-cyanopyridine (CeO₂ + 2-cyanopyridine system) drastically improves the DMC yield up to 94%, where the DMC yield in the absence of 2-cyanopyridine is only 0.7% [24a]. In this reaction system, hydration of 2-cyanopyridine gives 2-picolinamide, which is also catalyzed by CeO₂ (Eq. (2)) [28].



Toward the expansion of this catalyst system, we continued fundamental studies on the applicability and the reaction mechanism. This paper, thus, reports that various carbonates can be synthesized from CO₂, and the corresponding alcohols in the presence of CeO₂ and 2-cyanopyridine since the syntheses of carbonates except for DMC have hardly been reported and the yields based on alcohols are far from satisfactory (Table S1). In addition, the reaction mechanism is proposed on the basis of kinetic and isotopic studies, physicochemical analyses, and DFT calculation.

2. Experimental

2.1. Catalyst preparation

Preparation of CeO₂ catalyst was carried out by calcining commercially available cerium oxide HS (Daiichi Kigenso Kogyo Co. Ltd., Japan) for 3 h under air atmosphere at 873 K. The calcination temperature was optimized on the basis of the catalytic performance in the reaction of methanol + CO₂ with 2-cyanopyridine [24a]. The BET surface area of calcined CeO₂ was 84 m² g⁻¹.

2.2. Activity tests

All the reactions were carried out in an autoclave reactor with an inner volume of 190 ml. A typical procedure of the reaction of CO₂ + methanol with 2-cyanopyridine was as follows: 0.34 g of CeO₂ catalyst, 0.64 g of methanol (20 mmol, Wako Pure Chemical Industries, 99.8% min.), and 10.4 g of 2-cyanopyridine (100 mmol, Tokyo Chemical Industry Co., Ltd., 99.0% min.) were put into the autoclave together with a spinner, and then, the reactor was purged and pressurized with CO₂ (Shimakyu Co. Ltd., >99.5%). Gas line was closed, and then, the reactor was heated to the reaction temperature. The time when the temperature reached the desired reaction temperature is defined as zero reaction time. The mixture was constantly stirred during the reaction. After the

specific reaction time, the reactor was cooled to room temperature and the gas was collected. Ethanol (30 ml, Wako Pure Chemical Industries, 99.5% min.) and 1-hexanol (0.2 ml, Tokyo Chemical Industry Co., Ltd., 98.0% min.) were added to the liquid phase as a solvent and an internal standard substance for a quantitative analysis, respectively. Products in the liquid and gas phases were analyzed by using a gas chromatograph equipped with FID (Shimadzu GC-2014) and GC-MS (Shimadzu QP-2020) with a CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm).

For the synthesis of various carbonates from CO₂ and the corresponding alcohols, the procedures are the same as the case of the reaction of CO₂ + methanol with 2-cyanopyridine. After the reaction time, 30 ml of ethanol or acetone (Wako Pure Chemical Industries, 99.5% min.) was added to the liquid phase as a solvent, and 0.2 ml of 1-hexanol or 1-propanol (Wako Pure Chemical Industries, 99.5% min.) was added to the liquid phase as an internal standard substance for a quantitative analysis. The products in the liquid and gas phases were analyzed by gas chromatography equipped with an FID or quadrupole mass spectrometer (GC-MS) using a CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm) or TC-WAX capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25 μm).

2.3. Catalyst characterization and DFT calculation

The surface area of CeO₂ was measured with BET method (N₂ adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded by Rigaku Ultima IV with Cu K_α (40 kV, 40 mA) radiation. The thermogravimetric analysis (TG) and differential thermal analysis (DTA) data were collected under air using a Shimadzu DTG-60. A sample with the weight of 10 mg was charged into a Pt pan, and subsequently heated from room temperature to 873 K at a heating rate of 10 K/min.

DFT calculations of acidity and basicity were performed at B3LYP/6-311++G(d,p) level using Gaussian 03 program package.

2.4. Details of the reagents used in experiments

The details of the reactants are described below. All the chemicals were used without further purification. CO₂ (>99.5%) was purchased from Shimakyu Co. Ltd. Methanol (99.8% min.), ethanol (99.5% min.), 1-propanol (99.5% min.), 1-butanol (99.0% min.), 1-pentanol (98.0% min.), 1-octanol (98.0% min.), 1-decanol (95.0% min.), allyl alcohol (99.0% min.), benzyl alcohol (99.0% min.), 2-propanol (99.5% min.), acetonitrile (99.8% min.), acetamide (98.0% min.), 3-cyanopyridine (98.0% min.), 4-cyanopyridine (98.0% min.), pyridine (99.5% min.), piperidine (98.0% min.), benzoic acid (99.5% min.), benzonitrile (98% min.), benzamide (95% min.), and 2-furancarboxitrile (98.0% min.) were purchased from Wako Pure Chemical Industries. 2-Cyanopyridine (99.0% min.), 1-hexanol (98.0% min.), β-methyl alcohol (98.0% min.), 2-methyl-1-propanol (99.0% min.), cyclohexanemethanol (98.0% min.), cyanopyridine (97% min.), 2-pyrimidinecarbonitrile (98.0% min.), methylaminoacetonitrile (98% min.), (dimethylamino) acetonitrile (95% min.), 2-picolinamide (98.0% min.), and picolinic acid (99.0% min.) were purchased from Tokyo Chemical Industry Co., Ltd. Pyrrole-2-carboxitrile (96% min.) was purchased from Aldrich. 2-Pyridineacetonitrile (99% min.) and thiophene-2-carboxitrile (98% min.) were purchased from Alfa Aesar. 1H-Imidazole-4-carboxitrile was purchased from Tyger Scientific Inc.

In order to determine the retention time and molar sensitivity, commercially available reagents were used; dimethyl carbonate (98.0% min.), diethyl carbonate (98.0% min.), methyl carbamate (98.0% min.), ethyl carbamate (98.0% min.), butyl carbamate (98.0% min.), benzyl carbamate (98.0% min.), methyl picolinate

(98.0% min.), ethyl picolinate (98.0% min.), butyl 2-pyridinecarboxylate (90.0% min.), nicotinamide (98.0% min.), and isonicotinamide (99.0% min.) were purchased from Wako Pure Chemical Industries. Pyrazinecarboxamide (98.0% min.) was purchased from Tokyo Chemical Industry Co., Ltd. Di-*n*-propyl carbonate (99% min.), diallyl carbonate (99% min.), and *n*-propyl carbamate (98% min.) were purchased from Aldrich. 2-Pyridineacetamide (98% min.), thiophene-2-carboxamide (99% min.), 2-furamide (97% min.), dimethylallyl carbonate (97% min.), and dibenzyl carbonate (98% min.) were purchased from Alfa Aesar.

The retention time of di-*i*-propyl carbonate was determined by GC–MS. As this compound is not commercially available, di-*n*-propyl carbonate (Aldrich, 99.0% min.) was used for the determination of the molar sensitivity based on the same elemental compositions. In addition, the retention time of di-*n*-butyl carbonate, di-*n*-pentyl carbonate, di-*n*-hexyl carbonate, di-*n*-octyl carbonate, di-*n*-decyl carbonate, di-*i*-butyl carbonate, and bis(cyclohexylmethyl) carbonate was also determined by GC–MS. As these seven compounds are not commercially available, the yields of these carbonates were calculated by using the molar sensitivity of the corresponding alcohol. The retention time of the amides derived from pyrrole-2-carbonitrile, 1H-imidazole-4-carbonitrile, methylaminoacetonitrile, and (dimethylamino) acetonitrile was determined by GC–MS. As these four compounds are not commercially available, the yields of these amides were calculated by using the molar sensitivity of the corresponding nitriles. In addition, ¹H NMR spectra of these products were recorded on Bruker RTX-400 (400 MHz; CDCl₃; Me₄Si).

2.5. Procedure of the reaction of ¹⁸O-labeled methanol

¹⁸O-labeled methanol was purchased from Taiyo Nippon Sanso (95% min.). The reactions were carried out in an autoclave reactor with an inner volume of 70 ml. CeO₂ catalyst (0.03 g), ¹⁸O-labeled methanol (0.50 g), and 2-cyanopyridine (0 g or 0.87 g) were put into the autoclave together with a spinner, and then the reactor was purged and pressurized with CO₂ (5 MPa). Then the reactor was heated at the reaction temperature. After the reaction time, the reactor was cooled to room temperature, and acetone (50 ml) and 1-hexanol (0.2 ml) were added to the liquid phase as a solvent and an internal standard substance for a quantitative analysis, respectively. Products in the liquid and gas phases were analyzed by gas chromatography equipped with FID (Shimadzu GC-2014) and GC–MS (Shimadzu QP-2020) using a CP-Sil5 capillary column (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm).

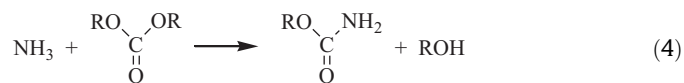
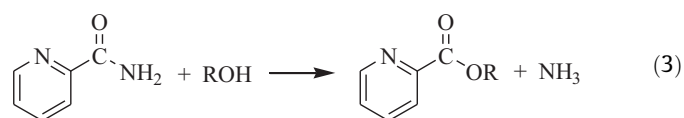
3. Results and discussion

3.1. Substrate scope of carbonate synthesis from CO₂ and alcohols

Various carbonate syntheses in the reaction of CO₂ + alcohol were examined over CeO₂ with 2-cyanopyridine. Alcohol conversions and DMC yields based on alcohol are shown in Table 1. Moreover, conversions and yields in hydration of 2-cyanopyridine are also shown in Table 1. Excess amount of 2-cyanopyridine was applied to achieve the high carbonate yields, although we have already reported that DMC can be obtained with 94% yield based on methanol even in the presence of stoichiometric amount of 2-cyanopyridine [24a]. The produced amide, 2-picolinamide, can be separated from the reaction mixture by extraction and can be readily restored to 2-cyanopyridine by dehydration of 2-picolinamide over Na₂O/SiO₂ catalyst [24a,24e]. Saturated linear alcohols (Entries 1–8) reacted to afford the corresponding carbonates in high yields (85–96%). It seems that the reactivity of alcohols decreases with longer alkyl chain. Note that the longer chain

alcohols (C2–C10), which are generally less reactive than methanol [15a,15b], were converted without loss of selectivity. The obtained yields based on alcohol are much higher than those reported in the literatures: the highest yields for ethanol, 1-propanol, and 1-butanol are 21% [24b], 17% [24b], and 3% [29], respectively. In addition, this paper is the first report on direct carbonate syntheses from CO₂ and 1-pentanol, 1-hexanol, 1-octanol, and 1-decanol. Furthermore, the reactions of unsaturated alcohols such as allyl alcohol (Entry 9) and β-methylallyl alcohol (Entry 10) proceeded to afford the corresponding carbonates in 76% and 51% yields, respectively. In the previous literature, allyl alcohol gave only 12% yield of the corresponding carbonate [20d], and there is no report on β-methylallyl alcohol. Sterically-bulky alcohols such as 2-methyl-1-propanol (Entry 11), benzyl alcohol (Entry 12), and cyclohexanemethanol (Entry 13) were also transformed to the corresponding carbonates in 60%, 74%, and 49% yields, respectively. There is no report on cyclohexanemethanol. The other carbonate yields are much higher than those in literatures (2-methyl-1-propanol: 7% [30] yield and benzyl alcohol: 5% yield [24b]). The reaction of 2-propanol (Entry 14), a secondary alcohol, gives the corresponding carbonate in 33% yield, which is higher than that of the previous report using benzonitrile as a dehydrating reagent (13% yield) [24b]. However, the present yield is much lower than those of primary alcohols. This tendency will be due to a steric hindrance rather than the thermodynamic limitation because DFT calculation (B3LYP/6-311++G(d,p), Table S2) showed that the energy change in the carbonate formation from CO₂ and 2-propanol (9.6 kJ mol⁻¹) is much smaller than that in hydration of 2-cyanopyridine to 2-picolinamide (–123.1 kJ mol⁻¹).

In all the reactions, less than 1 mmol of alkyl carbamate (<5% yield based on alcohol) and almost the same amount of alkyl picolinate as alkyl carbamate were detected as by-products. The formation of alkyl picolinate is attributed to the reaction of 2-picolinamide with alcohol (Eq. (3)), which co-produces NH₃. The further reaction of dialkyl carbonate with the product NH₃ gives alkyl carbamate (Eq. (4)).


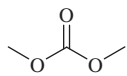

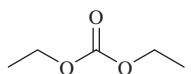
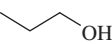
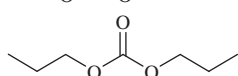
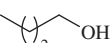
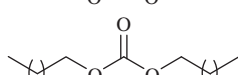
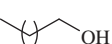
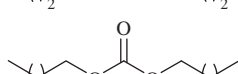
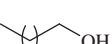
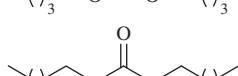
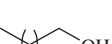
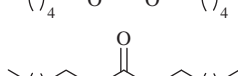
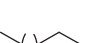
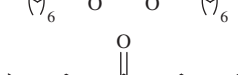
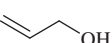
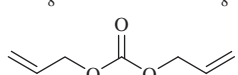
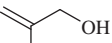
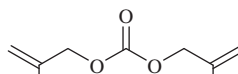
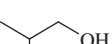
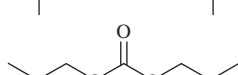
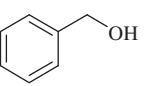
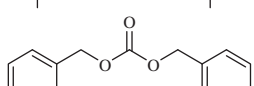
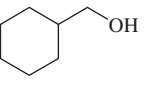
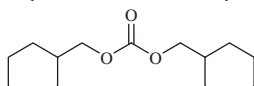
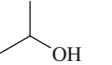
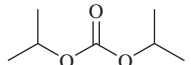


As above, the reaction system composed of CeO₂ + 2-cyanopyridine is quite effective for direct high-yield synthesis of various carbonates from CO₂ and alcohols. This catalyst system was denoted as CeO₂ + 2-cyanopyridine system in the following study.

3.2. Effect of reaction conditions

At first, the time dependence in DMC synthesis from CO₂ and methanol was studied as a model reaction with CeO₂ + 2-cyanopyridine system. Fig. 1 shows the results of time course under the standard conditions. The patterns of product distribution are almost the same as those reported in the previous paper [24a] using stoichiometric amount of 2-cyanopyridine. DMC was rapidly formed; 8.1 mmol of DMC was formed in 2 h and the initial turnover frequency (TOF) on the basis of total number of Ce is calculated to be 2.0 h⁻¹. Based on the number of Ce cations on the surface of CeO₂ (1.07 mmol g⁻¹) [28], TOF based on the surface Ce atom is 11 h⁻¹. DMC amount increased with increasing the reaction time and reached 9.6 mmol, which corresponds to 96% DMC yield based on methanol. The turnover number (TON) based on

Table 1
Synthesis of various carbonates from CO₂ and corresponding alcohols.

Entry	Alcohol	Carbonate	Temp. (K)	Time (h)	Alcohol conv. (%)	Carbonate yield (%) ^a	2-Cyanopyridine conv. (%)	2-Picolinamide yield (%) ^b
1			393	16	97	96	11	10
2			393	24	93	91	11	10
3			393	24	92	91	10	10
4			393	24	87	87 (79)	9.7	9.5
5			383	48	86	86	9.0	8.6
6			383	48	85	85	9.7	9.4
7			393	48	87	87	9.9	9.6
8			403	24	91	90 (82)	9.7	9.0
9			393	48	76	76	9.5	9.4
10			393	24	51	51	6.3	6.3
11			393	48	66	60	7.8	7.0
12			403	48	89	74	8.5	8.0
13			423	48	68	49	14	6.5
14			403	48	38	33	5.2	4.4

Reaction conditions: CeO₂ 0.34 g, Alcohol: 2-Cyanopyridine = 20 mmol: 100 mmol, CO₂ 5 MPa. The values in parentheses are the isolated yields.

^a Based on alcohol.

^b Based on 2-cyanopyridine.

total Ce and surface Ce atoms can be calculated to be 2.7 and 26. The high DMC yield in the present CeO₂ + 2-cyanopyridine system is mainly attributed to two reasons. The first one is that hydration of 2-cyanopyridine also proceeded to provide the corresponding amide stoichiometrically, resulting in complete removal of water from the reaction media and elimination of the limitation of chemical equilibrium. The second one is the property of 2-picolinamide. According to our previous works [24], amides that are produced by hydration of nitriles can inhibit the reaction. It should be noted that 2-picolinamide, which is the hydration product from 2-cyanopyridine, had no influence on the reaction. These effects will be discussed in Section 3.3.

Next, the effect of dehydrating reagents was examined. In this experiment, the molar ratio of methanol to nitrile was set to be large in order to compare the reaction rate precisely. The results are shown in Table 2. Without addition of any nitriles, the DMC yield under these conditions was 0.024% (Entry 15), which is far below the equilibrium (0.7%). The effect of nitriles was similar to the reported data [24a] which were obtained under stoichiometric ratio of methanol to nitrile and long reaction time. Addition of 2-cyanopyridine (Entry 1), pyrazine-2-carbonitrile (Entry 2), and 2-cyanopyrimidine (Entry 3) drastically increased the DMC yield up to 1.4%, 3.2%, and 1.8%, respectively. Among these nitriles, 2-cyanopyridine showed the highest selectivity to the amide

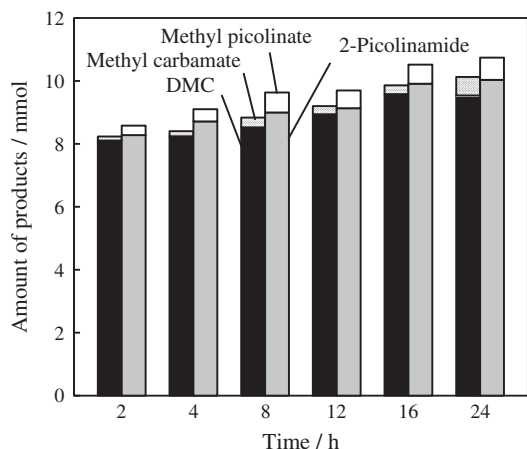


Fig. 1. Time course in the reaction of $\text{CH}_3\text{OH} + \text{CO}_2 + 2\text{-cyanopyridine}$. Reaction conditions: CeO_2 0.34 g, CH_3OH : 2-Cyanopyridine = 20 mmol: 100 mmol, CO_2 5 MPa, 393 K.

Table 2
DMC synthesis from CO_2 and methanol over CeO_2 with various nitriles

$$2\text{CH}_3\text{OH} + \text{CO}_2 + \text{Nitrile} \xrightarrow{\text{CeO}_2} \text{H}_3\text{CO}-\text{C}(=\text{O})-\text{OCH}_3 + \text{Amide}$$

Entry	Nitrile	Alcohol conv. (%)	DMC yield (%) ^a	Nitrile conv. (%)	Amide yield (%) ^b
1		1.7	1.4	16	15
2		9.0	3.2	36	3.7
3		11	1.8	25	2.4
4		1.2	0.039	11	9.6
5		1.4	0.043	9.9	9.1
6		7.3	0.052	9.3	0.3
7		14	0.000	1.8	<0.1
8		2.4	0.000	6.2	<0.1
9		3.5	0.028	9.6	<0.1
10		1.6	0.029	2.6	0.0
11		2.0	0.034	1.1	<0.1
12		0.5	0.000	<0.1	<0.1
13		1.8	0.034	5.0	0.8
14		0.2	0.006	2.3	0.0
15	None	1.0	0.024	-	-

Reaction conditions: CeO_2 0.01 g, CH_3OH : Additive = 200 mmol: 10 mmol, CO_2 5 MPa, 393 K, 1 h.

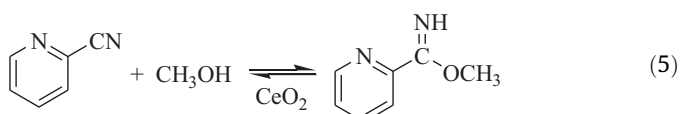
^a Based on alcohol.

^b Based on nitrile.

(94%). However, in the case of the other effective nitriles, the amide yields and selectivities were lower probably because of the side reactions such as reaction of the nitriles with methanol or decomposition of the nitriles. These results indicate that the addition of 2-cyanopyridine neither inhibits the reaction nor causes by-products. In contrast, the DMC yield was hardly improved in the presence of other nitriles (Entries 4–14). Although the structure of 2-pyridineacetonitrile (Entry 12) is similar to 2-cyanopyridine, DMC was hardly formed. According to the previous report, the hydration rate of 2-pyridineacetonitrile is quite low [28], which indicates that the distance between CN group and N atom in pyridine ring is important. This is probably due to the formation of intramolecular hydrogen bonding in the produced amide as described in the latter Section 3.3. These results and the reported data [24a] show that nitriles having a CN group at the 2-position relative to N atom of 6-membered ring heteroaromatics are effective as dehydrating reagents in DMC synthesis from CO_2 and methanol over CeO_2 . From these results, 2-cyanopyridine is the most effective dehydrating reagent, and the combination of CeO_2

with 2-cyanopyridine is the best system for the synthesis of organic carbonates. And also, these data show that DMC formation rate was enhanced by adding effective nitriles. Fig. 2 shows the initial time courses of DMC formation by CeO₂ + 2-cyanopyridine system and only CeO₂ system. DMC formation rates in CeO₂ + 2-cyanopyridine system and only CeO₂ system are estimated from the slopes of approximate curves to be 75 and 2.3 mmol g⁻¹ h⁻¹, respectively. As well as DMC yield [24a], the DMC formation rate was drastically enhanced by addition of 2-cyanopyridine.

The effect of CO₂ pressure was investigated in the ranges from 0.1 to 5 MPa, and the results are shown in Fig. 3. DMC yield increased with increasing CO₂ pressure. Moderate yield (61%) of DMC was obtained in the presence of 1 MPa of CO₂, and higher yield (82%) was achieved using 5 MPa of CO₂. Under low CO₂ pressure (0.1–1 MPa), methyl pyridine-2-carboximidate was detected as well as methyl picolinate and methyl carbamate. Methyl pyridine-2-carboximidate can be formed according to Eq. (5).



Actually, the formation of methyl pyridine-2-carboximidate was confirmed by the reaction of 2-cyanopyridine and methanol at 393 K under Ar atmosphere catalyzed by CeO₂ (Table S3). In contrast, the yields of methyl picolinate, methyl carbamate, and methyl pyridine-2-carboximidate were decreased with increasing CO₂ pressure. These by-products are produced by addition of alcohol as shown in Eqs. (3)–(5), and alcohol is known to be activated on acid–base pair sites of CeO₂ [31,32]. Taking into consideration that CO₂ can be strongly adsorbed on the acid–base pair sites of CeO₂, high pressure CO₂ will suppress the formation of these by-products by covering the active site of CeO₂. The formation of these compounds is not favorable for DMC synthesis since the addition of 1–5 mmol of methyl picolinate and methyl carbamate decreased the DMC formation rate (Table S4).

Fig. 4 shows the effect of the reaction temperature in the range from 373 to 413 K. DMC yield reached the maximum at 393 K. In the range of 373–393 K, DMC yield was increased with increasing the reaction temperature. In contrast, DMC yield was decreased with increasing the reaction temperature above 393 K. On the other hand, yields of by-products such as methyl carbamate and methyl picolinate were also increased above 393 K, which indicates that over-reactions and side reactions take place more easily

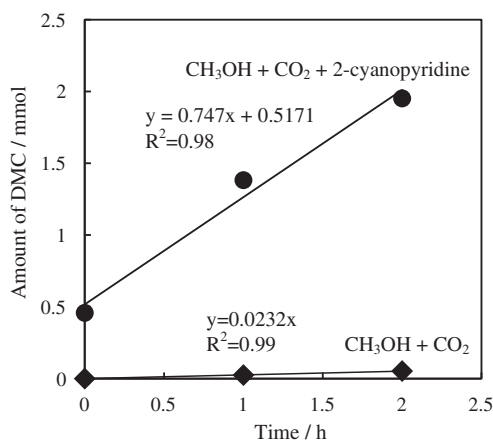


Fig. 2. Comparison of initial DMC formation rate in the reactions of (◆) CH₃OH + CO₂ and (●) CH₃OH + CO₂ + 2-cyanopyridine. Reaction conditions: CeO₂ 0.01 g, CH₃OH: 2-cyanopyridine = 200 mmol: (◆) 0 mmol or (●) 10 mmol, CO₂ 5 MPa, 393 K.

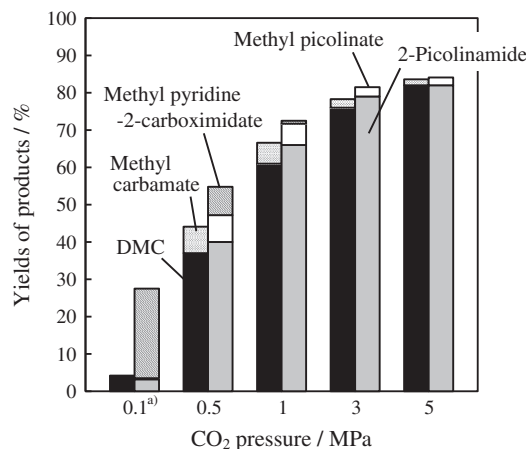


Fig. 3. Effect of CO₂ pressure in the reaction of CH₃OH + CO₂ + 2-cyanopyridine. Reaction conditions: CeO₂ 0.17 g, CH₃OH: 2-Cyanopyridine = 100 mmol: 50 mmol, 393 K, 24 h. (a) CO₂: Ar = 0.1 MPa: 0.9 MPa.

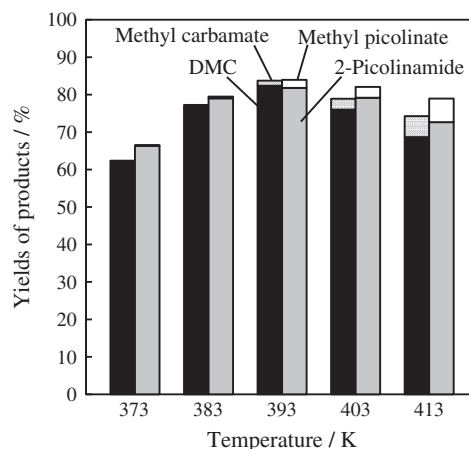
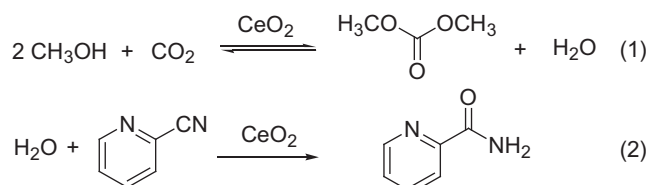


Fig. 4. Effect of reaction temperature in the reaction of CH₃OH + CO₂ + 2-cyanopyridine. Reaction conditions: CeO₂ 0.17 g, CH₃OH: 2-cyanopyridine = 100 mmol: 50 mmol, CO₂ 5 MPa, 12 h.

at higher temperatures. As these by-products suppress the formation of DMC, the optimal reaction temperature is determined to be 393 K.

3.3. Reaction mechanism of carboxylation of methanol and hydration of 2-cyanopyridine

In order to clarify the role of 2-cyanopyridine and the reaction mechanism of CeO₂ + 2-cyanopyridine system, kinetic and isotopic studies, physicochemical analyses and DFT calculation were conducted. As mentioned above, this reaction consists of two consecutive steps (Scheme 1): (1) carboxylation of methanol with CO₂ and (2) hydration of 2-cyanopyridine. First, hydration rate of



Scheme 1. DMC synthesis from CO₂ and methanol by CeO₂ + 2-cyanopyridine system: (1) carboxylation of methanol with CO₂ and (2) hydration of 2-cyanopyridine to 2-picolinamide.

2-cyanopyridine was measured by adding small amount of water in the present reaction conditions to determine which step is the rate-determining step. Here, 2-picolinamide and methyl picolinate were observed as products. The hydration rates were estimated by the total amount of 2-picolinamide and methyl picolinate because methyl picolinate is produced by the reaction of 2-picolinamide with alcohol (Eq. (3)). Fig. 5 shows the hydration rates as a function of amount of water, and the detailed data are shown in Fig. S1. The reaction rates were increased proportionally with increasing the amount of water, giving a good linearity between hydration rate and amount of H₂O. Therefore, the hydration rate in smaller amount of water can be estimated by exploration of the correlation line. The amount of H₂O in the actual reaction media will be almost zero because the hydration of 2-cyanopyridine effectively proceeds in this reaction system. Hence, 2-cyanopyridine hydration rate can be estimated to be at least 206 mmol g⁻¹ h⁻¹ by the y-intercept of Fig. 5, which is much larger than the DMC formation rate in CeO₂ + 2-cyanopyridine system (74 mmol g⁻¹ h⁻¹) under the similar reaction conditions. Therefore, hydration of 2-cyanopyridine proceeds even under low water concentration, and the rate-determining step is not hydration of 2-cyanopyridine but carboxylation of methanol with CO₂.

Next, the mechanism of carboxylation of methanol with CO₂ by CeO₂ + 2-cyanopyridine system was investigated. The kinetic studies about CO₂ pressure, amount of methanol and reaction temperature were carried out, and the results were compared with those in only CeO₂ system. DMC formation rates in CeO₂ + 2-cyanopyridine system were estimated by straight-line approximation below 30% of methanol conversions (Figs. S2–S4). On the other hand, in only CeO₂ system, DMC formation rates were estimated at methanol conversion lower than 0.1% since the equilibrium conversion of methanol is 0.7% in the CO₂ + methanol reaction.

The effect of CO₂ pressure on DMC formation rate was investigated in the range of 0.5–5 MPa as shown in Fig. 6 (the details are shown in Fig. S2). DMC formation rates in CeO₂ + 2-cyanopyridine system are almost constant under any CO₂ pressure, indicating that CO₂ pressure does not influence the DMC formation rate. This tendency in CeO₂ + 2-cyanopyridine system is similar to the case of only CeO₂ system.

Fig. 7 shows the effect of amount of methanol on DMC formation rate, and the details are shown in Fig. S3. In CeO₂ + 2-cyanopyridine system, the reaction order with respect to amount of methanol is nearby 1, which indicates that methanol is associated with the rate-determining step. This reaction order is also similar to that in only CeO₂ system.

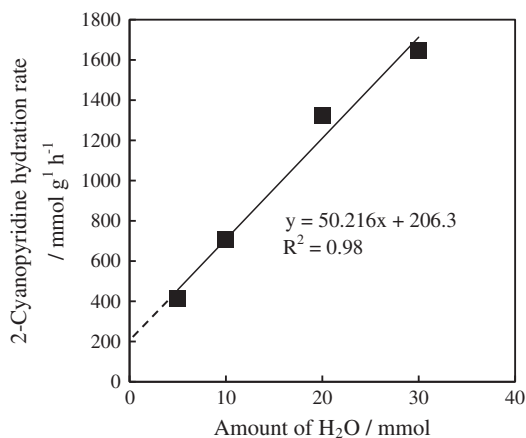


Fig. 5. Effect of the amount of H₂O in the reactions of CH₃OH + CO₂ + 2-cyanopyridine + H₂O. Reaction conditions: CeO₂ 0.001 g, CH₃OH: 2-cyanopyridine = 200 mmol: 10 mmol, CO₂ 5 MPa, 393 K, 0–1 h.

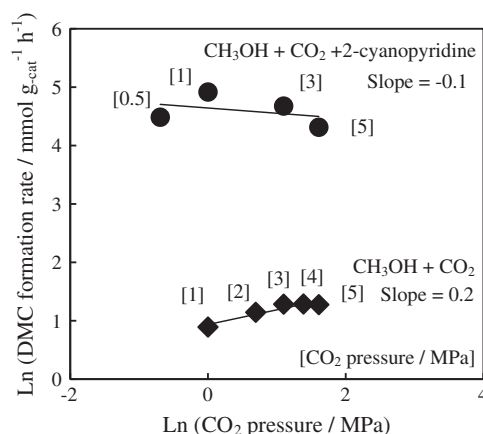


Fig. 6. Effect of CO₂ pressure in the reactions of (◆) CH₃OH + CO₂ and (●) CH₃OH + CO₂ + 2-cyanopyridine. Reaction conditions: (◆) CeO₂ 0.005–0.05 g, CH₃OH 200 mmol, 1–5 MPa, 393 K, 0–1.5 h, (●) CeO₂ 0.01 g, CH₃OH: 2-cyanopyridine = 200 mmol: 10 mmol, 0.5–5 MPa, 393 K, 0–2 h.

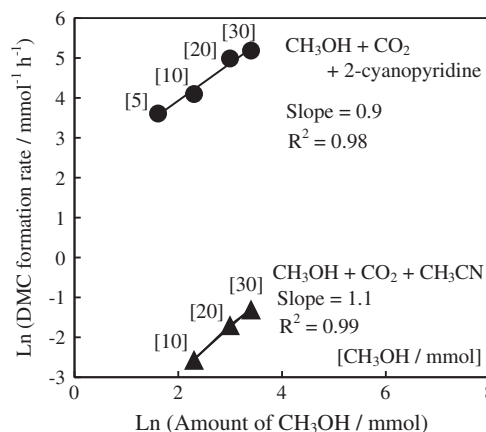


Fig. 7. Effect of the amount of methanol on DMC formation rate in the reactions of (▲) CH₃OH + CO₂ + CH₃CN and (●) CH₃OH + CO₂ + 2-cyanopyridine. Reaction conditions: (▲) CeO₂ 0.2 g, CH₃OH 10–30 mmol, CH₃CN 50 mmol, CO₂ 5 MPa, 393 K, 0–1 h, (●) CeO₂ 0.01 mg, CH₃OH 5–30 mmol, 2-cyanopyridine 50 mmol, CO₂ 5 MPa, 393 K, 0–1 h.

Fig. 8 shows the Arrhenius plots for CeO₂ + 2-cyanopyridine system and only CeO₂ system, and the details are shown in Fig. S4. The activation energies in CeO₂ + 2-cyanopyridine system and only CeO₂ system are estimated to be 72 and 73 kJ mol⁻¹, respectively, and the frequency factors for CeO₂ + 2-cyanopyridine system and only CeO₂ system are estimated to be 9.8 × 10¹¹ and 2.1 × 10¹⁰, respectively.

From the above kinetic studies for CeO₂ + 2-cyanopyridine system and only CeO₂ system, the dependence of DMC formation rate on CO₂ pressure and amount of methanol were almost the same in both systems, suggesting that the reaction mechanism of CeO₂ + 2-cyanopyridine system will be the same as that of only CeO₂ system. The reaction mechanism of DMC formation from methanol and CO₂ over CeO₂ has already been proposed based on the data of *in situ* FTIR [22g]. *In situ* FTIR analyses were carried out with methanol and/or CO₂ by changing CO₂ pressures (0.1, 0.5, 5 MPa). The reaction mechanism is as follows (Scheme 2): (i) methanol is dissociated on CeO₂ to form two types of methoxy adspecies on CeO₂ (terminal methoxy adspecies (CH₃O–Ce) and bridged methoxy adspecies). This is supported by the previous reports on methanol adsorption over CeO₂ by FTIR [31,32,28], (ii) Adsorbed CO₂ on CeO₂ is not inserted to bridged methoxy adspecies but to terminal methoxy adspecies (CH₃O–Ce) to form Ce-methyl carbonate

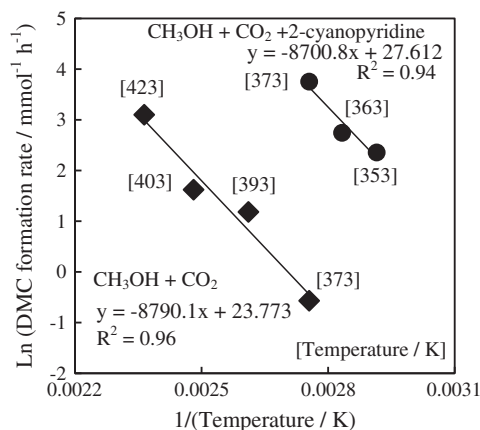
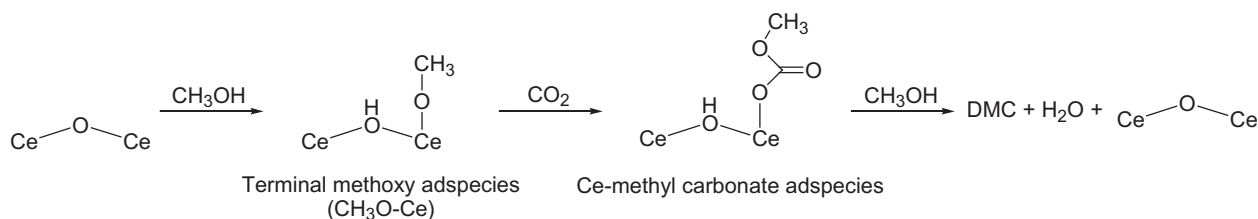


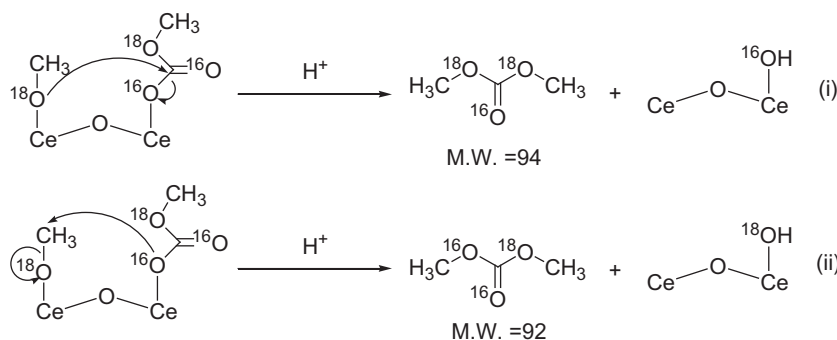
Fig. 8. Arrhenius plots of the reactions of (◆) $\text{CH}_3\text{OH} + \text{CO}_2$ and (●) $\text{CH}_3\text{OH} + \text{CO}_2 + 2\text{-cyanopyridine}$. Reaction conditions: (◆) CeO_2 0.01–0.05 g, CH_3OH 200 mmol, CO_2 5 MPa (at a reaction temperature), 373–423 K, 0–1 h, (●) CeO_2 0.01 mg, CH_3OH : 2-cyanopyridine = 200 mmol: 10 mmol, CO_2 5 MPa (at a reaction temperature), 353–373 K, 0–1 h.

adspecies as shown by that terminal methoxy adspecies on CeO_2 were quickly decreased even when 0.1 MPa CO_2 was introduced. The Ce-methyl carbonate adspecies can be regarded as an important intermediate for the reaction. (iii) DMC is formed by the reaction between Ce-methyl carbonate and another methanol on CeO_2 , which is the rate-determining step. Therefore, the reaction mechanism of $\text{CeO}_2 + 2\text{-cyanopyridine}$ system will follow this reaction mechanism.

In the above reaction mechanism, the rate-determining step is the reaction of methanol with Ce-methyl carbonate adspecies on CeO_2 , which is supported by the results of the effect of methanol amount (Fig. 7). However, the detailed mechanism for the rate-determining step is not sufficiently elucidated, and two mechanisms have been proposed on CeO_2 as follows (Scheme 2): (i) nucleophilic addition of methoxy species to Ce-methyl carbonate



Scheme 2. Proposed reaction mechanism of DMC synthesis from CO_2 and methanol [22g].



Scheme 3. DMC formation by two different mechanisms and difference of molecular weight of DMC using ^{18}O -labeled methanol: (i) nucleophilic addition of methoxy species to Ce-methyl carbonate species, (ii) electrophilic addition of methyl species to Ce-methyl carbonate species.

species and (ii) electrophilic addition of methyl species to Ce-methyl carbonate species [22g,24,33]. In order to confirm which of these two mechanisms is true, the reaction test was conducted using ^{18}O -labeled methanol. Based on that a molecular weight of unlabeled DMC is 90, if the nucleophilic addition of methoxy species to carbonate adspecies would be the main route, the intensity of mass number (m/z) 94 is more strongly detected than that of 92 (Scheme 3-(i)). In contrast, electrophilic addition of methyl species gives the opposite tendency (Scheme 3-(ii)). In $\text{CeO}_2 + 2\text{-cyanopyridine}$ system, at 31% conversion of $\text{CH}_3^{18}\text{OH}$, the intensity ratio of $m/z = 94$ to $m/z = 92$ was 4.2 (the mass spectrum is shown in Fig. 9). This result indicates that two methoxy species of DMC are mainly derived from methanol (Scheme 3-(i)). The same results were obtained in only CeO_2 system (the intensity ratio of $m/z = 94$ to $m/z = 92$ was 3.6 at 0.8% conversion (Fig. S5)). Therefore, this step proceeds via nucleophilic addition of methoxy species to Ce-methyl carbonate species on CeO_2 .

The mechanism of the nitrile hydration was also examined. From the results of the effect of water amount (Fig. 5), the reaction order with respect to amount of water is 0.8 (Fig. S6). Taking into consideration that water can be easily dissociated to OH species and proton on CeO_2 [28], addition of OH species on CeO_2 to nitrile will be the rate-determining step in nitrile hydration. On the other hand, the effective nitriles have the following structure: CN group is at the 2-position relative to N atom of 6-membered ring heteroaromatics. In addition, the basicity of pyridine is higher than that of CN group. Since CeO_2 has only Lewis acid sites as acid sites, 2-cyanopyridine is adsorbed on the Lewis acid sites of CeO_2 at the N atom of heteroaromatics. These reaction tendencies are almost the same as those in hydration of 2-cyanopyridine over CeO_2 in water proposed in the previous reports [28], where the hydration proceeds via adsorption of 2-cyanopyridine followed by addition of OH species on CeO_2 to the nitrile group of 2-cyanopyridine. Therefore, in $\text{CeO}_2 + 2\text{-cyanopyridine}$ system, hydration of 2-cyanopyridine will proceed in the same manner.

Finally, the influence of the amide, which is produced by hydration of nitrile, was studied. In order to achieve high yields

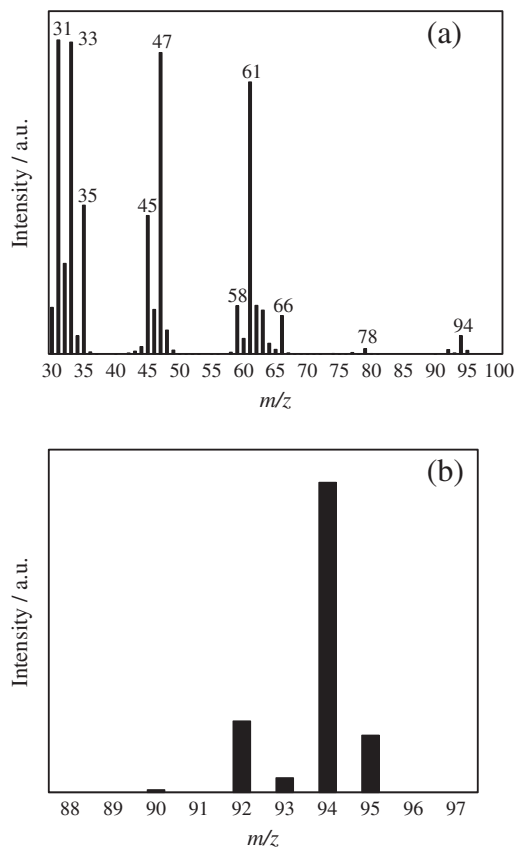


Fig. 9. Mass spectrum of DMC formed by $\text{CH}_3\text{OH} + \text{CO}_2 + 2\text{-cyanopyridine}$ (a) $m/z = 30\text{--}100$, (b) $m/z = 88\text{--}97$. Reaction conditions: 70 ml autoclave, CeO_2 0.03 g, CH_3OH : 2-cyanopyridine = 15.6 mmol: 8.37 mmol, CO_2 5 MPa, 393 K, 2 h. Result of reaction test: CH_3OH conversion 31%, DMC yield 31%, 2-cyanopyridine conversion 31%, 2-picolinamide yield 30%.

of carbonates from CO_2 and alcohols using nitrile as a dehydrating reagent, the weak interaction of the corresponding hydrated products, amide with CeO_2 surface can be essential. In our previous work, DMC synthesis over CeO_2 with benzonitrile as a dehydrating reagent afforded low DMC yield (47%) [24b], implying deactivation of CeO_2 by covering the CeO_2 surface with the produced amide. In contrast, in $\text{CeO}_2 + 2\text{-cyanopyridine}$ system, high yield (96%) was achieved. In order to clarify the difference of dehydrating ability

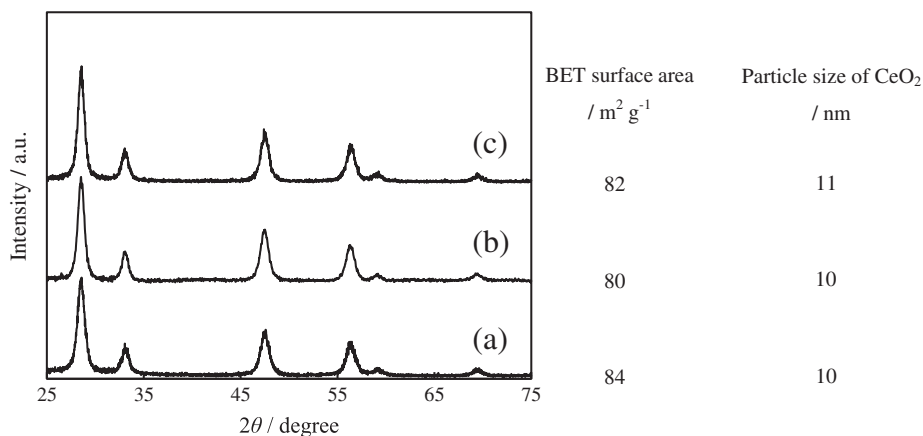


Fig. 10. XRD pattern and BET surface area before and after the reaction: (a) Fresh CeO_2 , (b) CeO_2 after the reaction with benzonitrile, (c) CeO_2 after the reaction with 2-cyanopyridine. Reaction conditions: CeO_2 0.17 g, CH_3OH : $\text{C}_6\text{H}_5\text{CN} = 100$ mmol: 200 mmol, CO_2 1 MPa, 423 K, 2 h or CeO_2 0.17 g, CH_3OH : 2-Cyanopyridine = 100 mmol: 50 mmol, CO_2 5 MPa, 393 K, 2 h. The particle size of CeO_2 was determined by XRD patterns.

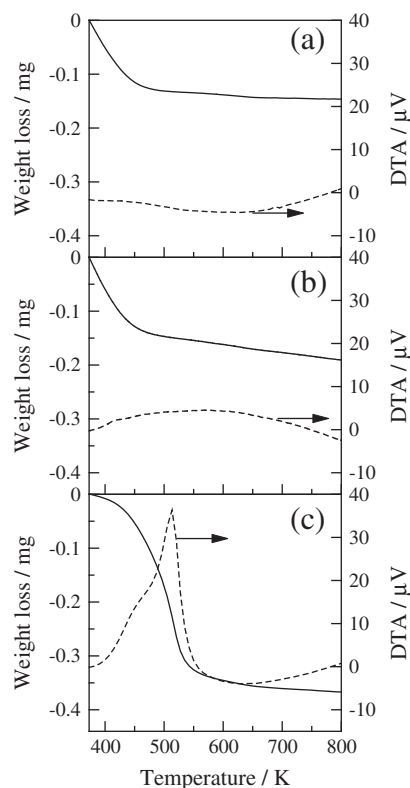
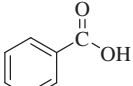
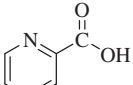
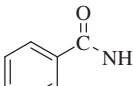
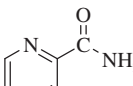
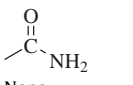


Fig. 11. TG-DTA profiles of CeO_2 before the reaction (Fresh) (a) and after the reaction with 2-cyanopyridine (b) and benzonitrile (c). Reaction conditions: CeO_2 0.17 g, CH_3OH : 2-cyanopyridine = 200 mmol: 100 mmol, CO_2 5 MPa, 393 K, 2 h.

between 2-cyanopyridine and benzonitrile, XRD, BET surface area, and TG-DTA analyses were conducted. XRD and BET surface area analyses were examined using CeO_2 before and after the reaction with 2-cyanopyridine and benzonitrile (Fig. 10). BET surface areas and XRD profiles were unchanged before and after the both reactions with 2-cyanopyridine and benzonitrile, which suggests that the structure of CeO_2 is very stable under the reaction conditions and nitriles give no influence on the structure of CeO_2 . Next, TG-DTA analyses were conducted using CeO_2 before and after the reaction with 2-cyanopyridine and benzonitrile (Fig. 11). CeO_2 before the reaction showed weight loss of about 0.14 mg (~ 1.4 wt%), but hardly showed an exothermic signal, suggesting

Table 3

The acidity and the initial DMC formation yield in the reaction of $\text{CH}_3\text{OH} + \text{CO}_2 + \text{additive}$.

Entry	Additive	Energy change in deprotonation (kJ mol^{-1}) ^a	Initial rate ^b ($\text{mmol g}^{-1} \text{h}^{-1}$)
1	Benzoic acid 	+1448	0.0
2	Picolinic acid 	+1467	0.0
3	Benzamide 	+1511	0.0
4	2-Picolinamide 	+1549	2.5
5	Acetamide 	+1564	2.3
6	None	-	2.3

^a B3LYP/6-311++G(d,p).

^b Reaction conditions: CeO_2 0.01 g, CH_3OH : Additive = 200 mmol: 10 mmol, CO_2 5 MPa, 393 K, 1 h.



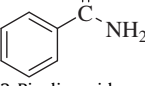
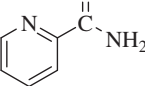

that adsorbed H_2O or CO_2 on CeO_2 will be desorbed (Fig. 11-(a)). Similarly, CeO_2 with 2-cyanopyridine presented almost the same tendency (weight loss ~ 0.18 mg) (Fig. 11-(b)). In contrast, CeO_2 with benzonitrile provided larger weight loss of about 0.36 mg (~ 3.6 wt%) and a large DTA signal around 500 K. The signal can be assigned to the corresponding amide [24a,24b]. Assuming that all the weight loss except the weight loss of fresh CeO_2 is derived from the corresponding amides, the amount of adsorbed amides on CeO_2 with 2-cyanopyridine and benzonitrile were calculated to be about 0.5 and 2.8 $\mu\text{mol}/\text{m}^2_{\text{CeO}_2}$, respectively. Considering that 2.6 $\mu\text{mol}/\text{m}^2_{\text{CeO}_2}$ of CO_2 can be adsorbed on CeO_2 [34], benzamide will cover the entire adsorption sites of CeO_2 surface. In addition, in FTIR spectra of CeO_2 after the reaction of $\text{CH}_3\text{OH} + \text{CO}_2 + \text{C}_6\text{H}_5\text{CN}$ the intensities of the bands assigned to benzamide increased with increasing the reaction time (Fig. S7). These results indicate that 2-picolinamide is hardly adsorbed on CeO_2 , in contrast, benzamide is more strongly adsorbed than 2-picolinamide. In addition, these results are supported by the addition experiments of 2-picolinamide and benzamide in the reaction media as described below (Table 3). A small amount of benzamide completely blocked the active sites of CeO_2 . However, 2-picolinamide has no influence on the reaction.

Furthermore, as previously reported [24a], CeO_2 can be recycled at least three times without loss of activity and selectivity.

The difference of dehydrating ability between 2-cyanopyridine and benzonitrile can be attributed to the difference of adsorption properties between the corresponding amides (2-picolinamide and benzamide). The amide can be adsorbed on the acid and/or base sites of CeO_2 , which will be the active ones of CeO_2 for carboxylation of alcohol and hydration of nitriles. Therefore, acidity and basicity of the amides will influence the adsorption strength on CeO_2 . Acidity and basicity were calculated by DFT calculations using these amides and the related compounds, benzoic acid,

Table 4

The basicity and the initial DMC formation yield in the reaction of $\text{CH}_3\text{OH} + \text{CO}_2 + \text{additive}$.

Entry	Additive	Energy change in deprotonation (kJ mol^{-1}) ^a	Initial rate ^b ($\text{mmol g}^{-1} \text{h}^{-1}$)
1	Piperidine 	-989	0.0
2	Pyridine 	-966 (py site)	2.4
3	Benzamide 	-922 (=O site)	0.0
4	2-Picolinamide 	-922 (py site) -909 (=O site)	2.5
5	Acetamide 	-894 (=O site)	2.3
6	-	-	2.3

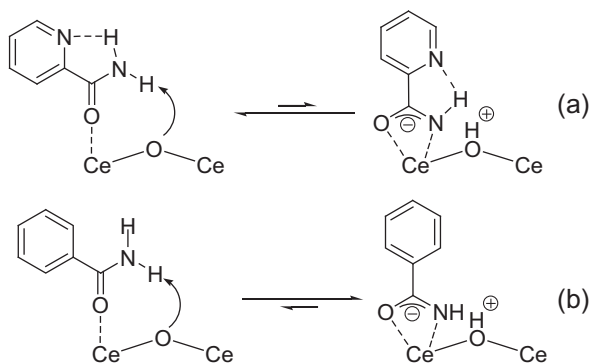
^a B3LYP/6-311++G(d,p).

^b Reaction conditions: CeO_2 0.01 g, CH_3OH : Additive = 200 mmol: 10 mmol, CO_2 5 MPa, 393 K, 1 h.

picolinic acid, and acetamide for acidity, and piperidine, pyridine, and acetamide for basicity. The relation between acidity/basicity of the compounds and the reaction rates was examined.

Table 3 lists DMC formation rate in the reaction of methanol and CO_2 with additives and the energy change in deprotonation of the additives calculated by DFT. Here, acidity of compounds is lower with increasing the value of the energy change. In the absence of any additives, DMC formation rate is 2.3 $\text{mmol g}^{-1} \text{h}^{-1}$ (Entry 6). Addition of carboxylic acids such as benzoic acid (Entry 1) and picolinic acid (Entry 2) completely suppressed the DMC formation (~ 0.0 $\text{mmol g}^{-1} \text{h}^{-1}$), and the energy changes in deprotonation are +1448 and +1467 kJ mol^{-1} for benzoic acid and picolinic acid, respectively, which are regarded as strong acidic compounds. In addition, DMC was not detected even in the presence of benzamide (Entry 3), where the energy change in deprotonation is +1511 kJ mol^{-1} . On the other hand, the addition of 2-picolinamide (Entry 4) and acetamide (Entry 5) did not affect DMC formation rate, showing higher energy changes in deprotonation of +1549 and +1564 kJ mol^{-1} , respectively, which means that the acidity of these amides is comparatively low. Therefore, the strong acidic compound is a strong catalyst poison for the reaction.

Table 4 lists the relation between the DMC formation rate and the energy change in protonation of additives, where the basicity of compounds is higher with decreasing the value of energy change. In the absence of any additives, DMC formation rate is 2.3 $\text{mmol g}^{-1} \text{h}^{-1}$ (Entry 6). Addition of piperidine did not give DMC (Entry 1) and the value of energy change in protonation of piperidine is -989 kJ mol^{-1} , which represents strong basicity. In contrast, the addition of pyridine (Entry 2) did not show any effect on DMC formation rate, and the value of energy change in protonation is -966 kJ mol^{-1} and the basicity of pyridine is lower than that of piperidine. However, addition of benzamide completely



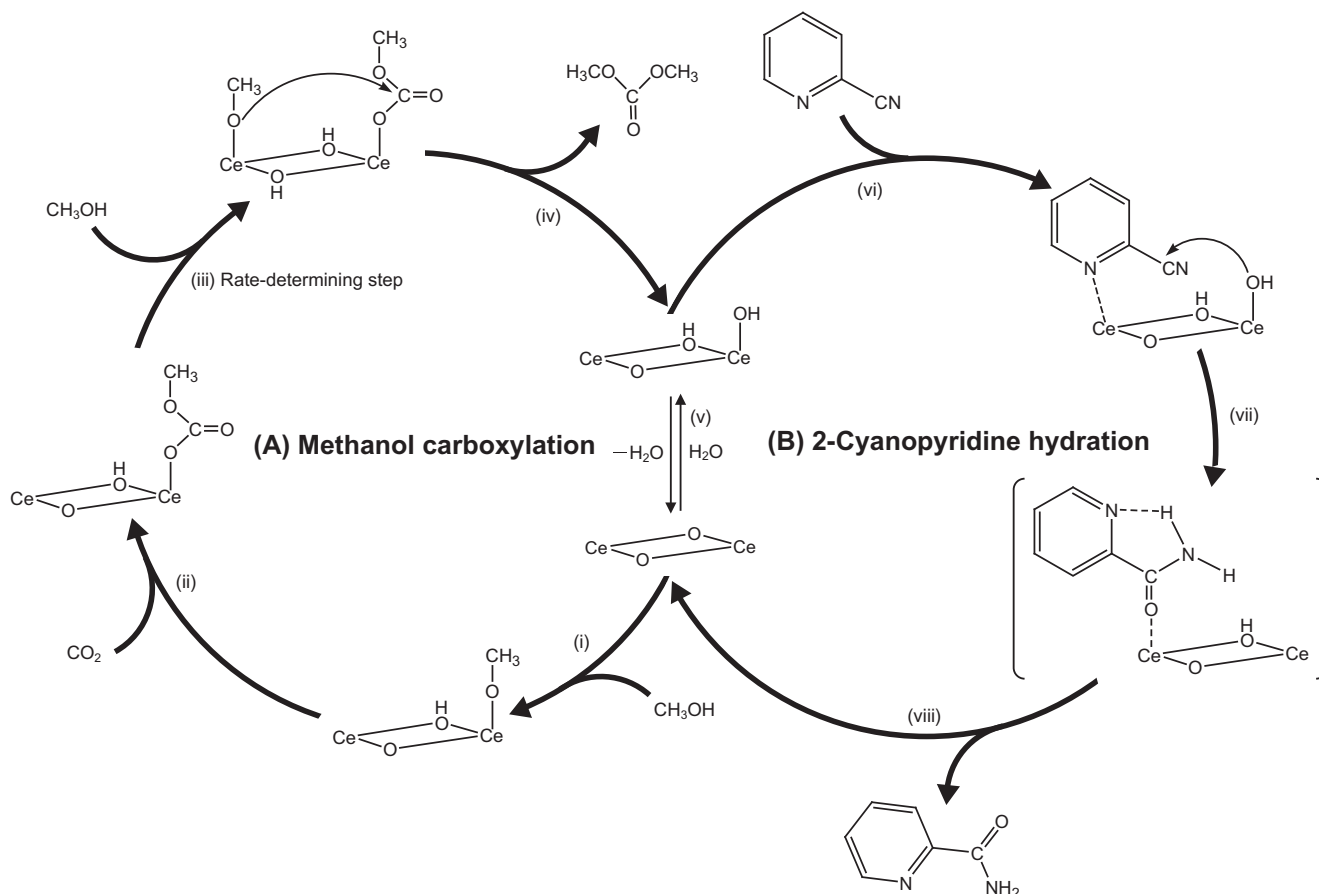
Scheme 4. Adsorption state of 2-picolinamide (a) and benzamide (b) on CeO_2 .

prohibited the DMC formation (Entry 3), which can be explained by its acidity as shown in Table 3. The addition of 2-picolinamide (Entry 4) and acetamide (Entry 5) has no effect on DMC formation rate and these compounds are much less basic than pyridine and benzamide. These results indicate that basicity of benzamide does not mainly contribute to the poisoning of CeO_2 .

From these results, acidity of benzamide mainly influenced the deactivation of CeO_2 , and this is connected to the strong basicity of CeO_2 . It is well known that carboxylic acid can be adsorbed on CeO_2 as a form of carboxylate by proton extraction of carboxyl group. The proposed adsorption models of 2-picolinamide and benzamide are shown in Scheme 4. Extraction of H atom of the amide group in 2-picolinamide is difficult because of an intramolecular hydrogen bonding between H atom in the amide group and N atom of the

pyridine ring (Scheme 4-(a)) [35] because of low acidity of 2-picolinamide. On the other hand, extraction of H atom of the amide group in benzamide will be easy by the basic sites of CeO_2 to form stable amide anion species on CeO_2 , which will be very stable on CeO_2 (Scheme 4-(b)). As a result, the difference of dehydrating ability between 2-cyanopyridine and benzonitrile can be attributed to the difference of adsorption strength on CeO_2 between the corresponding amides, 2-picolinamide, and benzamide. The difference of adsorption strength is generated by the difference of acidity between the amides, which can be derived from the presence or absence of the intramolecular hydrogen bonding between H atom of amide group and N atom of pyridine ring.

Based on these results and discussion, the proposed mechanism is shown in Scheme 5. The cycle of methanol carboxylation begins with the adsorption of methanol (A). Methanol is adsorbed on CeO_2 and forms $\text{CH}_3\text{O}-\text{Ce}$ and gives $\text{Ce}-\text{methyl carbonate species}$ (i). CO_2 is successively inserted into $\text{CH}_3\text{O}-\text{Ce}$ and gives $\text{Ce}-\text{methyl carbonate species}$ (ii). Another methanol is adsorbed on CeO_2 to give $\text{CH}_3\text{O}-\text{Ce}$ species (iii). Nucleophilic addition of methoxy species of $\text{CH}_3\text{O}-\text{Ce}$ to provide DMC, which is confirmed by the experiment using ^{18}O -labeled methanol, and CeO_2 is regenerated (iv). On the other hand, the cycle of 2-cyanopyridine hydration is as follows (B). 2-Cyanopyridine interacts CeO_2 with N atom in pyridine ring (vi). Cyano group of adsorbed 2-cyanopyridine is attacked by OH species on CeO_2 and to form 2-picolinamide adspecies (vii). 2-Picolinamide species can be rapidly desorbed from CeO_2 surface (viii). If water exists in the reaction media, water is easily dissociated on CeO_2 (v). The rate determining step of the whole system is nucleophilic addition of methoxy group to carbonate adspecies on CeO_2 . Considering that the reaction rate was enhanced in $\text{CeO}_2 + 2\text{-cyanopyridine}$ system,



Scheme 5. Reaction mechanism of DMC formation from $\text{CH}_3\text{OH} + \text{CO}_2 + 2\text{-cyanopyridine}$.

2-cyanopyridine will play an important role of activating methanol or carbonate adspecies on CeO₂. We are now investigating the details of the rate enhancement mechanism.

4. Conclusion

CeO₂ + 2-cyanopyridine system is effective for the synthesis of organic carbonates from CO₂ and alcohols, and various organic carbonates can be obtained in high yields (up to 96% yield). Although carbonate yields are generally limited by the reaction equilibrium, addition of 2-cyanopyridine drastically improved the carbonates yields by removal of water from the reaction media. Investigation of various nitriles as dehydrating reagents revealed that the effective nitrile as a dehydrating reagent is one having a CN group at the 2-position relative to N atom of 6-membered ring heteroaromatics. The adsorption of the produced amides on CeO₂ can poison the active sites of CeO₂. However, the amides produced from effective nitriles can form an intramolecular hydrogen bonding between H atom in amide group and N atom in pyridine ring, which leads to reduction in the acidity of the amides and makes the adsorption on CeO₂ weak. According to kinetic studies in the presence and absence of 2-cyanopyridine, the reaction mechanism is unchanged and 2-cyanopyridine works as an excellent dehydrating reagent. The hydration of 2-cyanopyridine is very fast and carboxylation of methanol with CO₂ proceeds via two times nucleophilic addition of methoxy group on CeO₂. The rate determining step is the nucleophilic addition of second methoxy group to Ce-methyl carbonate species, which is supported by the reaction using ¹⁸O-labeled methanol.

Acknowledgments

A part of this research is funded by the Cabinet Office, Government of Japan through its “Funding Program for Next Generation World-leading Researchers”.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2014.07.022>.

References

- [1] a C. Genovese, C. Ampelli, S. Perathoner, G. Centi, *J. Energy Chem.* 22 (2013) 202;
b G.A. Olah, G.K.S. Prakash, A. Goepfert, *J. Am. Chem. Soc.* 133 (2011) 12881;
c E.A. Quadrelli, G. Centi, J.L. Duplan, S. Perathoner, *ChemSusChem* 4 (2011) 1194;
d M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T.E. Müller, *ChemSusChem* 4 (2011) 1216;
e T. Sakakura, J.C. Choi, H. Yasuda, *Chem. Rev.* 107 (2007) 2365;
f M. Aresta, *Carbon Dioxide as Chemical Feedstock*, WILEY-VCH, 2010;
g C. Song, *Catal. Today* 115 (2006) 2.
- [2] a J.F. Hull, Y. Himeda, W.H. Wang, B. Hashiguchi, R. Periana, D.J. Szalda, J.T. Muckerman, E. Fujita, *Nat. Chem.* 4 (2012) 383;
b R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* 131 (2009) 14168;
c P.G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* 99 (1999) 475;
d P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* 118 (1996) 344.
- [3] a M. Murakami, K. Maeda, Y. Goto, *Jpn. Kokai Tokkyo Koho JP2010-194421A*;
b F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, *J. Catal.* 249 (2007) 185;
c J. Toyir, P.R. de la Piscina, J.L.G. Fierro, N. Homs, *Appl. Catal. B* 34 (2001) 255;
d O.S. Joo, K.D. Jung, I. Moon, A.Y. Rozovskii, G.I. Lin, S.H. Han, S.J. Uhm, *Ind. Eng. Chem. Res.* 38 (1999) 1808;
e A. Bansode, A. Urakawa, *J. Catal.* 309 (2014) 66.
- [4] a X.B. Lu, D.J. Darensbourg, *Chem. Soc. Rev.* 41 (2012) 1462;
b M. North, R. Pasquale, C. Young, *Green. Chem.* 12 (2010) 1514;
c A. Decortes, A.M. Castilla, A.W. Kleij, *Angew. Chem. Int. Ed.* 49 (2010) 9822;
d D.J. Darensbourg, *Chem. Rev.* 107 (2007) 2388;
e M.L. Man, K.C. Lam, W.N. Sit, S.M. Ng, Z. Zhou, Z. Lin, C.P. Lau, *Chem. Eur. J.* 12 (2006) 1004;
f J. Sun, S. Fujita, M. Arai, *J. Organomet. Chem.* 690 (2005) 3490.
- [5] a M. Tamura, M. Honda, K. Noro, Y. Nakagawa, K. Tomishige, *J. Catal.* 305 (2013) 191;
b M. Honda, S. Sonehara, H. Yasuda, Y. Nakagawa, K. Tomishige, *Green Chem.* 13 (2011) 3406;
c A. Ion, C.V. Dooslaer, V. Parvulescu, P. Jacobs, D.D. Vos, *Green Chem.* 10 (2008) 111;
d M. Abila, J.C. Choi, T. Sakakura, *Green Chem.* 6 (2004) 524;
e M. Abila, J.C. Choi, T. Sakakura, *Chem. Commun.* (2001) 2238.
- [6] a Y. Ono, *Appl. Catal. A* 155 (1997) 133;
b A.A. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [7] a S.H. Pyo, P. Persson, M.A. Mollaahmad, K. Sørensen, S. Lundmark, R. Hattika, *Pure Appl. Chem.* 84 (2012) 637;
b S. Fukuoka, I. Fukawa, M. Tojo, K. Oonishi, H. Hachiya, M. Aminaka, K. Hasegawa, K. Komiya, *Catal. Surv. Asia* 14 (2010) 146.
- [8] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* 4 (2011) 3243.
- [9] a S. Grego, F. Aricò, P. Tundo, *Pure Appl. Chem.* 84 (2012) 685;
b P. Tundo, F. Aricò, A.E. Rosamilia, M. Rigo, A. Maranzana, G. Tonachini, *Pure Appl. Chem.* 81 (2009) 1971.
- [10] M.A. Pacheco, C.L. Marshall, *Energy Fuels* 11 (1997) 2.
- [11] T. Shimomura, M. Miura, *Jpn. Kokai Tokkyo Koho* 60-197639A.
- [12] a Y. Yamamoto, *Catal. Surv. Asia* 14 (2010) 103;
b D. Delledonne, F. Rivetti, U. Romano, *J. Organomet. Chem.* 488 (1995) C15.
- [13] C.Y. Hao, S. Wang, X. Ma, *J. Mol. Catal. A* 306 (2009) 130.
- [14] a A. Pylrik, W.F. Hoelderich, K. Müller, W. Arlt, *J. Strautmman, D. Kruse, Appl. Catal. B* 125 (2012) 486;
b L. Wang, Y. Wang, S. Liu, L. Liu, X. Ma, Y. Deng, *Catal. Commun.* 16 (2011) 45.
- [15] a J. Kadokawa, H. Habu, S. Fukamachi, M. Karasu, H. Tagaya, K. Chiba, *J. Chem. Soc., Perkin Trans. 1* (1999) 2205;
b Y. Yamazaki, K. Kakuma, Y. Du, S. Saito, *Tetrahedron* 66 (2010) 9675;
c D. Chaturvedi, N. Mishra, V. Mishra, *Tetrahedron Lett.* 48 (2007) 5043.
- [16] M.A. Casadei, S. Cesa, M. Feroci, A. Inesi, *New J. Chem.* 23 (1999) 433.
- [17] a Y. Nakagawa, K. Tomishige, *Catal. Surv. Asia* 15 (2011) 111;
b A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 1502;
c T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, *J. Catal.* 240 (2006) 213;
d Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.* 1 (2011) 179;
e Y. Nakagawa, M. Tamura, K. Tomishige, *J. Mater. Chem. A* 2 (2014) 6688.
- [18] a M. Schlaf, *Dalton Trans.* (2006) 4645;
b H.P. Luo, W.D. Xiao, *Chem. Eng. Sci.* 56 (2001) 403.
- [19] Y. Amada, S. Koso, Y. Nakagawa, K. Tomishige, *ChemSusChem* 3 (2010) 728.
- [20] a M.P. Kalhor, H. Chermette, D. Ballivet-Tkatchenko, *Polyhedron* 32 (2012) 73;
b M.P. Kalhor, H. Chermette, S. Chambrey, D.B. Tkatchenko, *Phys. Chem. Chem. Phys.* 13 (2011) 2401;
c T. Sakakura, K. Kohno, *Chem. Commun.* (2009) 1312;
d K. Kono, J.C. Choi, Y. Ohshima, H. Yasuda, T. Sakakura, *ChemSusChem* 1 (2008) 186;
e M. Aresta, A. Dibenedetto, C. Pastore, I. Pápai, G. Schubert, *Top. Catal.* 40 (2006) 71;
f M. Aresta, A. Dibenedetto, E. Fracchiolla, P. Giannoccaro, C. Pastore, I. Pápai, G. Schubert, *J. Org. Chem.* 70 (2005) 6177;
g J. Kizlink, *Collect. Czech Chem. Commun.* 60 (1995) 687;
h J. Kizlink, *Collect. Czech Chem. Commun.* 58 (1993) 1399.
- [21] a N. Kumar, E. Leino, P.M. Arvela, A. Aho, M. Kaldström, M. Tuominen, P. Laukkanen, K. Eränen, J.P. Mikkola, T. Salmi, D.Y. Murzin, *Micropor. Mesopor. Mater.* 152 (2012) 71;
b D. Ballivet-Tkatchenko, J.H.Z. dos Santos, K. Philippot, S. Vasireddy, *C. R. Chim.* 14 (2011) 780;
c D. Ballivet-Tkatchenko, F. Bernard, F. Demoisson, L. Plasseraud, S.R. Sanapureddy, *ChemSusChem* 4 (2011) 1316;
d V. Eta, P.M. Arvela, J. Wärna, T. Salmi, J.P. Mikkola, D.Y. Murzin, *Appl. Catal. A* 404 (2011) 39;
e V. Eta, P.M. Arvela, E. Salminen, T. Salmi, D.Y. Murzin, J.P. Mikkola, *Catal. Lett.* 141 (2011) 1254;
f V. Eta, P.M. Arvela, A.R. Leino, K. Kordás, T. Salmi, D.Y. Murzin, J.P. Mikkola, *Ind. Eng. Chem. Res.* 49 (2010) 9609;
g A. Aouissi, A.W. Apblett, Z.A. Al-Othman, A. Al-Amro, *Trans. Met. Chem.* 35 (2010) 927;
h M. Aresta, A. Dibenedetto, C. Pastore, A. Angelini, B. Aresta, I. Pápai, *J. Catal.* 269 (2010) 44;
i D. Aymes, D.B. Tkatchenko, K. Jeyalakshmi, L. Saviot, S. Vasireddy, *Catal. Today* 147 (2009) 62;
j M. Aresta, A. Dibenedetto, C. Pastore, C. Cuocci, B. Aresta, S. Cometa, E.D. Giglio, *Catal. Today* 137 (2008) 125;
k B. Fan, J. Zhang, R. Li, W. Fan, *Catal. Lett.* 121 (2008) 297;
l K.W. La, I.K. Song, *React. Kinet. Catal. Lett.* 89 (2006) 303;
m L.A. Allaoui, A. Aouissi, *J. Mol. Catal. A* 259 (2006) 281;
n C.F. Li, S.H. Zhong, *Catal. Today* 82 (2003) 83.
- [22] a K. Tomishige, T. Sakaihorii, Y. Ikeda, K. Fujimoto, *Catal. Lett.* 58 (1999) 225;
b K. Tomishige, Y. Ikeda, T. Sakaihorii, K. Fujimoto, *J. Catal.* 192 (2000) 355;
c Y. Ikeda, T. Sakaihorii, K. Tomishige, K. Fujimoto, *Catal. Lett.* 66 (2000) 59;
d Y. Ikeda, M. Asadullah, K. Fujimoto, K. Tomishige, *J. Phys. Chem. B* 105 (2001) 10653;
e K. Tomishige, Y. Furusawa, Y. Ikeda, M. Asadullah, K. Fujimoto, *Catal. Lett.* 76 (2001) 71;
f K. Tomishige, K. Kunimori, *Appl. Catal. A* 237 (2002) 103;

- g Y. Yoshida, Y. Arai, S. Kado, K. Kunimori, K. Tomishige, *Catal. Today* 115 (2006) 95.
- [23] a K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kunimori, *Catal. Lett.* 95 (2004) 45;
b K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kunimori, *Green Chem.* 6 (2004) 206.
- [24] a M. Honda, M. Tamura, Y. Nakagawa, S. Sonehara, K. Suzuki, K. Fujimoto, K. Tomishige, *ChemSusChem* 6 (2013) 1341;
b M. Honda, S. Kuno, S. Sonehara, K. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, *ChemCatChem* 3 (2011) 365;
c M. Honda, S. Kuno, B. Noorjahan, K. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, *Appl. Catal. A* 384 (2010) 165;
d M. Honda, A. Suzuki, B. Noorjahan, K. Fujimoto, K. Suzuki, K. Tomishige, *Chem. Commun.* (2009) 4596;
e M. Honda, M. Tamura, Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.* 4 (2014) 2830;
f M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* 4 (2014) 1893.
- [25] a A. Dibenedetto, M. Aresta, A. Angelini, J. Ethiraj, B.M. Aresta, *Chem. Eur. J.* 18 (2012) 10324;
b E. Leino, P. Mäki-Arvela, K. Eränen, M. Tenho, D.Yu. Murzin, T. Salmi, J.P. Mikkola, *Chem. Eng. J.* 176–177 (2011) 124.
- [26] T. Sakakura, J.C. Choi, Y. Saito, T. Masuda, T. Sako, T. Oriyama, *J. Org. Chem.* 64 (1999) 4506.
- [27] a W. Lei, H. Xiaolong, L. Jiding, Z. Xia, C. Jian, *Sep. Sci. Technol.* 46 (2011) 1396;
b W. Won, X. Feng, D. Lawless, *Sep. Purif. Technol.* 31 (2003) 129.
- [28] a M. Tamura, H. Wakasugi, K. Shimizu, A. Satsuma, *Chem. Eur. J.* 17 (2011) 11428;
b M. Tamura, A. Satsuma, K. Shimizu, *Catal. Sci. Technol.* 3 (2013) 1386.
- [29] D.T. Nowlan, C.V. McNeff, US Patent US2011288309A1.
- [30] Y. Inaba, T. Onuki, K. Naito, *Jpn. Kokai Tokkyo Koho JP2012140355A*.
- [31] a M. Tamura, T. Tonomura, K. Shimizu, A. Satsuma, *Green Chem.* 14 (2012) 984;
b M. Tamura, T. Tonomura, K. Shimizu, A. Satsuma, *Green Chem.* 14 (2012) 717.
- [32] a L.C. Lavalley, *Catal. Today* 27 (1996) 377;
b A. Badri, C. Binet, J.C. Lavalley, *J. Chem. Soc. Faraday Trans.* 93 (1997) 1159.
- [33] a R. Juárez, P. Concepción, A. Corma, H. García, *Chem. Commun.* 46 (2010) 4181;
b R. Juárez, A. Corma, H. García, *Green Chem.* 11 (2009) 949.
- [34] S. Sato, R. Takahashi, T. Sodesawa, K. Matsumoto, Y. Kamimura, *J. Catal.* 184 (1999) 180.
- [35] D.S. Marlin, M.M. Olmstead, P.K. Mascharak, *J. Mol. Struct.* 554 (2000) 211.