Catalytic conversion of carbon dioxide into dimethyl carbonate using reduced copper-cerium oxide catalysts as low as 353 K and 1.3 MPa and the reaction mechanism

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INTRODUCTION
Carbon dioxide is one of major green house gases. The conversion of CO₂ has been widely investigated to reduce the atmospheric concentration of CO₂ (Izumi, 2013). In the viewpoint of global warming, fixation methods of CO₂ and/or converted compounds from CO₂ are also critical. Transferring captured CO₂ to the bottom of the sea in a supercritical state is partially in practical use, but it incurs huge investment costs. The conversion of CO₂ to dimethyl carbonate (DMC) is attractive because DMC can be used as an electrolytic solution of lithium ion battery, methylating reagent, and feedstock for engineering plastics (Ono, 1997).

DMC has been conventionally synthesized starting from phosphine, carbon monoxide, or oxirane, but these materials are toxic and/or explosive. From CO₂ and methanol/acetals, DMC was synthesized using homogeneous Sn catalysts at 10–30 MPa and 353–453 K (Sakakura et al., 1998, 1999, 2000; Kalhor et al., 2011) and using homogeneous Ni catalysts at 353 K and 1.0 Mpa (Shi et al., 2013). Catalyst separation was improved for DMC synthesis using heterogeneous CeO₂ (Yoshida et al., 2006), ZrO₂ (Tomishige et al., 1999), solid solution of ZrO₂ and CeO₂ (Tomishige et al., 2001; Zhang et al., 2011b), Ga₃O₃/Co₀ₓZr₀ₓO₂ (Lee et al., 2011), CeₓZr₀.₉₋ₓY₀.₁O₂ (Zhang et al., 2011a), SmOₓ–ZrO₂/SiO₂ (Ballivet-Tkatchenko et al., 2011), Cu₁₋ₓPW₁₂O₄₀ (Aouissi et al., 2010), H₃PW₁₂O₄₀/CeₓTi₁₋ₓO₂ (La et al., 2007), Cu–KF/MgSiO (Li and Zhong, 2003), Cu–Ni–diatomite (Chen et al., 2012), Cu–Ni–graphite (Bian et al., 2009a), Cu–Ni–V₂O₅–active carbon (Bian et al., 2009b), and Cu–Ni–V₂O₅–SiO₂ (Wu et al., 2006; Wang et al., 2007) at 353–453 K and 0.1–60 MPa. The conversion of methanol to DMC was as much as 7.9% for 24 h (Zhang et al., 2011b). In the viewpoint of global environment and the reduction of CO₂, it is desirable to synthesize DMC from CO₂ under mild reaction conditions.

In future, the DMC synthesis reported in this work could be combined with photocatalysis to synthesize DMC from CO₂ as a single starting material.
MATERIALS AND METHODS
PREPARATION OF CeO2
Cerium oxide samples were prepared from cerium nitrate hexahydrate (Wako Pure Chemical, >98.0%). It was dissolved in deionized water (<0.06 μS cm⁻¹) to make the concentration to 0.2 mol L⁻¹. A 5% ammonia aqueous solution (Wako Pure Chemical) was added to the solution to reach the pH 10. Obtained yellow precipitate was filtered using a polytetrafluoroethylene-based membrane filter (Omnipore JGWP04700, Millipore) with a pore size of 0.2 μm and washed several times with deionized water. The obtained powder was calcined in air at 673 K for 4 h. Then, the size of 0.2 μm and washed several times with deionized water. The obtained powder was calcined in air at 673 K for 4 h. Then, the size of 0.2 μm was added to the solution to reach the pH 10. Obtained yellow precipitate was filtered using a polytetrafluoroethylene-based membrane filter (Omnipore JGWP04700, Millipore) with a pore size of 0.2 μm and washed several times with deionized water. The obtained powder was calcined in air at 673 K for 4 h. Then, the powder was connected to a vacuum system using rotary and diffusion pumps (10⁻⁶ Pa) and the temperature was elevated at a ramping rate of 5 K min⁻¹ from 290 to 673 K and kept at 673 K for 1 h.

A part of freshly-prepared CeO2 above was reduced under 25 kPa of hydrogen. The temperature was elevated from 290 to 673 K with the ramping rate of 10 K min⁻¹ and maintained at 673 K for 1 h.

PREPARATION OF Cu–CeO2
3.8–950 mg of copper nitrate trihydrate (Wako Pure Chemical, >99.9%) was dissolved in 10 mL of deionized water. The Cu²⁺ solution was added to 1.0 g of CeO2 powder prepared in section Preparation of CeO2. Then, 25% of ammonia aqueous solution was added to the suspension until the pH reached 9.5. The mixture was reacted at 290 K for 1 h with magnetically stirred at a rate of 300 rpm. The color of precipitate was yellow, yellow green, and dark brown when the Cu content was 0.1, 1, and 20 wt%, respectively. The precipitate was filtered using JGWP04700 membrane and washed by several times with deionized water. The obtained powder was dried at 353 K for 12 h and denoted Cu–CeO2. The Cu–CeO2 samples were treated under H2 (25 kPa). The temperature was elevated from 290 to 673 K with the ramping rate of 10 K min⁻¹, maintained at 673 K for 1 h, and evacuated (10⁻⁶ Pa) at 673 K for 30 min.

CHARACTERIZATION
Nitrogen adsorption isotherm measurements were performed at 77 K within the pressure range 1.0–90 kPa in a vacuum system connected to diffusion and rotary pumps (10⁻⁶ Pa) and equipped with a capacitance manometer (Models CCMT-1000A and GM-2001, ULVAC). The Brunauer-Emmett-Teller (BET) surface area (S BET) was calculated on the basis of eight-point measurements between 10 and 46 kPa (P/P0 = 0.10–0.45) on the adsorption isotherm. The sample was evacuated at 423 K for 90 min before the measurements.

The electronic state of cerium in catalysts was investigated by the synchrotron X-ray measurements. The catalyst powder samples were prepared in vacuum (10⁻⁶ Pa) and transferred directly to a Pyrex glass cell equipped with 50 μm-thick Kapton (Dupont) windows on both sides. The samples in N2 (60 kPa) or CO2 gas (60 kPa) were sealed with fire and transported to beamline.

Ce L3-edge X-ray absorption fine structure (XAFS) spectra were measured at 290 K in a transmission mode in the Photon Factory at the High-Energy Accelerator Research Organization (Tsukuba, Japan) on beamline 9C and also in SPring-8 (Sayo, Japan) on beamline 01B1. The X-ray energy was calibrated at the first intense peak top energy (5731.1 eV) for the Ce L3-edge spectrum of CeO2. The XAFS data were analyzed with a software package XDAP version 2.2.7 (Vaarkamp et al., 2006).

RESULTS
DMC SYNTHESIS FROM CO2 AND METHANOL

Pretreatment effects in H2
In the test under the 2.8 MPa CO2 (initial pressure) at 393 K for 6 h, DMC formation rate using incipient CeO2 catalyst was 0.44 mmol h⁻¹ gcat⁻¹ and that for reduced CeO2 was 0.70 mmol h⁻¹ gcat⁻¹ (Table 1A). Total initial pressure of CO2 and methanol was 3.5 MPa at 393 K. By the pretreatment effect in H2 at 673 K, the synthesis rate increased by a factor of 1.6 times. The conversion (%) of methanol to DMC was defined as

\[
\text{Conversion} = \frac{2 \times \text{molar amount of DMC formed}}{\text{molar amount of methanol introduced}} \times 100.
\]

Effects of the Cu addition
The DMC synthesis rate using reduced Cu–CeO2 (0.5 wt% Cu) was compared to that using reduced CeO2 at 393 K for 2 h. The rates were 1.8 and 1.5 mmol h⁻¹ gcat⁻¹, respectively (Table 1B). By the inclusion of 0.5 wt% of Cu in the catalyst, the rate increased by a factor of 1.2 times. The conversion of methanol to DMC was improved to 0.32% (Table 1B).

Next, the effects of Cu addition were investigated by progressively changing the Cu content between 0 and 20 wt% under...
Table 1 | Conditions and results of DMC synthesis from methanol and CO₂ over Ce oxide and Cu-promoted Ce oxide catalysts¹.

| Entry | Condition | Cu content (wt%) | Reaction T. (K) | Reaction time (h) | CO₂ at 290 K (MPa) | Methanol at Reac. T. (MPa) | Total at Reac. T. (MPa) | Yield (mmol) | Synthesis rate (mmol h⁻¹ g₉cat⁻¹) | Conversion to methanol (%) |
|-------|-----------|------------------|----------------|------------------|-------------------|----------------------|------------------------|-------------|-----------------------------------|--------------------------|
|       |           |                  |                |                  |                   |                      |                        |             |                                   |                          |
| (A) PRETREATMENT EFFECTS IN H₂ |
| a     | Incipient | 0                | 393            | 6                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.29                              | 0.44                     | 0.24                     |
| b     | Reduced   | 0                | 393            | 6                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.41                              | 0.70                     | 0.33                     |
|       |           |                  |                |                  |                   |                      |                        |             |                                   |                          |                          |
| (B) Cu EFFECTS AT HIGHER PRESSURE |
| c     | Reduced   | 0                | 393            | 2                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.33                              | 1.5                      | 0.27                     |
| d     | Reduced   | 0.5              | 393            | 2                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.40                              | 1.8                      | 0.32                     |
|       |           |                  |                |                  |                   |                      |                        |             |                                   |                          |                          |
| (C) Cu EFFECTS AT LOWER PRESSURE |
| e     | Reduced   | 0                | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.087                             | 0.41                     | 0.071                    |
| f     | Reduced   | 0.1              | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.19                              | 0.95                     | 0.15                     |
| g     | Reduced   | 0.3              | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.13                              | 0.64                     | 0.10                     |
| h     | Reduced   | 0.5              | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.13                              | 0.60                     | 0.11                     |
| i     | Reduced   | 1                | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.088                             | 0.43                     | 0.071                    |
| j     | Reduced   | 5                | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.079                             | 0.41                     | 0.064                    |
| k     | Reduced   | 10               | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.038                             | 0.19                     | 0.031                    |
| l     | Reduced   | 20               | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.078                             | 0.39                     | 0.063                    |
|       |           |                  |                |                  |                   |                      |                        |             |                                   |                          |                          |
| (D) REACTION PRESSURE EFFECTS |
| d     | Reduced   | 0.5              | 393            | 2                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.40                              | 1.8                      | 0.32                     |
| m     | Reduced   | 0.5              | 393            | 2                | 1.0               | 1.4                  | 0.64                   | 2.0         | 0.18                              | 0.79                     | 0.14                     |
| h     | Reduced   | 0.5              | 393            | 2                | 0.50              | 0.67                  | 0.64                   | 1.3         | 0.13                              | 0.60                     | 0.11                     |
| n     | Reduced   | 0.5              | 393            | 2                | 0.10              | 0.13                  | 0.64                   | 0.77        | <0.003                           | <0.015                   | <0.002                   |
| o     | Reduced²  | 0.1              | 403            | 2                | 3.6               | 5.8                  | 0.84                   | 6.6         | 0.29                              | 3.1                      | 0.23                     |
| p     | Reduced²  | 0.5              | 403            | 2                | 3.6               | 5.8                  | 0.84                   | 6.6         | 0.22                              | 1.9                      | 0.17                     |
|       |           |                  |                |                  |                   |                      |                        |             |                                   |                          |                          |
| (E) REACTION TEMPERATURE EFFECTS |
| d     | Reduced   | 0.5              | 393            | 2                | 2.0               | 2.8                  | 0.64                   | 3.5         | 0.40                              | 1.8                      | 0.32                     |
| q     | Reduced   | 0.5              | 373            | 2                | 2.0               | 2.6                  | 0.35                   | 2.9         | 0.056                             | 0.24                     | 0.045                    |
| r     | Reduced   | 0.5              | 353            | 2                | 2.0               | 2.5                  | 0.18                   | 2.7         | 0.006                             | 0.031                    | 0.005                    |

¹² Catalyst charged: 100 mg except for entries o and p (50 mg).
lower initial pressure (0.67 MPa) of CO$_2$ at 393 K. By the inclusion of 0.1 wt% of Cu in Cu–CeO$_2$ catalyst, the DMC synthesis rate increased 2.3-fold higher: from 0.41 mmol h$^{-1}$ g$_{\text{cat}}^{-1}$ (reduced CeO$_2$) to 0.95 mmol h$^{-1}$ g$_{\text{cat}}^{-1}$ (Table 1C; Figure 1). However, further increase of Cu content between 0.3 and 1 wt% in Cu–CeO$_2$ catalyst was not effective compared to the test results for the Cu–CeO$_2$ catalyst, 0.1 wt% of Cu (Table 1C). When the Cu content was between 1 and 20 wt%, the synthesis rates gradually approached to constant, similar to the one for undoped CeO$_2$ (0.41 mmol h$^{-1}$ g$_{\text{cat}}^{-1}$) (Table 1C; Figure 1).

**Reaction pressure effects**

In the reaction tests at 393 K using reduced Cu–CeO$_2$ catalyst (0.5 wt% Cu), partial pressure of CO$_2$ introduced at 290 K was varied between 2.0 and 0.10 MPa. The partial (initial) pressure of CO$_2$ increased to between 2.8 and 0.13 MPa at reaction temperature of 393 K (Table 1D). The DMC synthesis rates were plotted as a function of initial pressure of CO$_2$ and initial total pressure of CO$_2$+ methanol at 393 K (Figure 2). The DMC synthesis was possible under the total pressure of 1.3 MPa, but the amount of produced DMC was below detection limit (3 μmol) under the total pressure of 0.77 MPa at 393 K (Table 1D). The DMC synthesis rates were proportional to partial pressure of CO$_2$ (Figure 2).

The reaction pressure effects were also tested under severer reaction conditions: at 403 K and 6.6 MPa using Cu–CeO$_2$ catalysts (0.1 and 0.5 wt% Cu) (Table 1o,p). The synthesis rates (3.1–1.9 mmol h$^{-1}$ g$_{\text{cat}}^{-1}$) were higher by a factor of 3.3–3.2 times compared to corresponding test results at 393 K and 1.3 MPa (Table 1C,D). Thus, major reason of relatively low DMC synthesis rates in this paper was mild reaction conditions at 393–353 K and 3.5–1.3 MPa.

**Reaction temperature effects**

Further, the reaction temperature was varied between 393 and 353 K using reduced Cu–CeO$_2$ catalyst (0.5 wt% Cu) under the CO$_2$ partial pressure of 2.0 MPa introduced at 290 K. The CO$_2$ pressure increased to between 2.8 and 2.5 MPa at reaction temperatures of 393–353 K (Table 1E). Under the total pressure of 2.7 MPa, DMC synthesis was possible as low as 353 K: 0.031 mmol h$^{-1}$ g$_{\text{cat}}^{-1}$ (Table 1E; Figure 3). The apparent activation energy was estimated to 120 kJ mol$^{-1}$ based on the Arrhenius plot (Figure 3, inset).

**BET SURFACE AREA AND Ce L$_3$-EDGE XANES**

The BET surface area was 78 and 94 m$^2$ g$_{\text{cat}}^{-1}$ for Cu–CeO$_2$ samples consisting of 0.1 and 0.5 wt% Cu, respectively (Table 2). Ce L$_3$-edge XANES spectra taken for Ce–based catalysts and also standard Ce compounds were depicted in Figure 4. Twin peaks appeared at 5731 and 5738 eV in the XANES spectrum for as-synthesized CeO$_2$ (spectrum a), indicating that valence state of Ce$^{4+}$ was predominant (Zhang et al., 2004).

When the CeO$_2$ was reduced under hydrogen at 673 K (spectrum b), a shoulder peak gradually grew at 5727 eV, on the lower side of peak at 5731 eV. As an intense whiteline peak appeared at 5726.7 eV in the spectrum for Ce(NO$_2$)$_3$·6H$_2$O (Figure 4A-f), the shoulder peak for spectrum b suggested the partial reduction of initial Ce$^{4+}$ to Ce$^{3+}$. The partial reduction of CeO$_2$ is traditionally known to promote electron-donating catalysis, e.g., ammonia synthesis (Izumi et al., 1996; Aika et al., 1997). The spectrum b was fitted with the spectrum a for fresh CeO$_2$ and spectrum f for Ce(NO$_2$)$_3$·6H$_2$O by changing the mixing ratio of standard spectra (Izumi and Nagamori, 2000; Izumi et al.,
FIGURE 3 | DMC synthesis rates over Cu–CeO2 catalyst (0.5 wt% of Cu) at 393–353 K. Initial partial pressure of CO2 was 2.0 MPa at 290 K. (Inset) The associated Arrhenius plot and the fit to the equation.

| Cu content (wt%) | \(S_{\text{BET}}\) (m² gcat⁻¹) |
|------------------|-------------------------|
| 0.1              | 78                      |
| 0.5              | 94                      |

Table 2 | BET surface area of Cu–promoted Ce oxide catalysts.

2007). Spectra a and f were used as models of Ce⁴⁺ and Ce³⁺ states, respectively. The goodness of fit was evaluated based on the residual-factor \(R_f\)

\[
R_f = \frac{\int |\chi_{\text{sample data}}(k) - \chi_{\text{reference data}}(k)|^2 \, dk}{\int |\chi_{\text{sample data}}(k)|^2 \, dk}
\]

The spectrum b was best fitted with the mixing ratio of Ce⁴⁺:Ce³⁺ = 90:10 (Figure 4B-b).

The shoulder peak at 5727 eV also appeared in the XANES spectrum for reduced Cu–CeO2 (0.5 wt% Cu; spectrum c), and the intensity was greater than that in spectrum b for reduced CeO2. The spectrum c was also fitted with the spectrum a (Ce⁴⁺) and spectrum f (Ce³⁺) by changing the mixing ratio. The best fit was realized with the mixing ratio was Ce⁴⁺:Ce³⁺ = 85:15 (Figure 4B-c).

The Ce L₃-edge XANES spectrum for reduced Cu–CeO2 catalyst (0.1 wt% Cu; spectrum d) was essentially identical with that for reduced CeO2 catalyst (spectrum b). The best-fit ratio with the mixing standard spectrum component of Ce⁴⁺ and Ce³⁺ was 90 and 10%. However, the shoulder peak at 5727 eV in the spectrum significantly weakened when 60 kPa of CO2 was introduced to the reduced Cu–CeO2 (0.1 wt% Cu) at 290 K (spectrum e). The best-fit ratio with the mixing standard spectrum component of Ce⁴⁺ and Ce³⁺ was 95 and 5%. The decrease of shoulder peak intensity at 5727 eV suggested re-oxidation of Ce³⁺ to Ce⁴⁺ by the reaction with CO2.

DISCUSSION

DMC SYNTHESIS UNDER Milder CONDITIONS

DMC synthesis from CO2 and methanol was reported at a synthesis rate of 1.8–5.1 mmol h⁻¹ gcat⁻¹ using CeO2 at 403 K and 8.7 MPa for 2–4 h (Yoshida et al., 2006). DMC synthesis rate from CO2 and methanol in this work using reduced CeO2 at 393 K and 3.5 MPa for 6 h was lower: 0.70 mmol h⁻¹ gcat⁻¹ (Table 1A) due to lower reaction temperature and lower pressure. Because the forward reaction reduces the molar amount of materials in system from three to two and is uphill reaction (Pacheco and Marshall, 1997) (Equation 1), reaction conditions of lower reaction temperature and lower pressure are disadvantageous for the DMC synthesis reaction. The synthesis rate was enhanced by a factor of 1.6 times by the pre-reduction in H2 for CeO2 (Table 1A).

\[
\text{CO}_2 + 2\text{CH}_3\text{OH} \rightleftharpoons \text{OC(CHOCH}_3)_2 + \text{H}_2\text{O}
\]

\[
\Delta G_r = 51.0 \text{ kJ mol}^{-1} (373 \text{K})
\]  \tag{1}

The disadvantage of moderate reaction conditions was compensated by the Cu addition to CeO2 catalysts. At 393 K and 3.5 MPa for 2 h, the DMC synthesis rates increased to 1.8 mmol h⁻¹ gcat⁻¹ by the addition of 0.5 wt% of Cu (Table 1B).

The effects of Cu addition to the DMC synthesis rates were compared at even milder reaction conditions: at 393 K and 1.3 MPa for 2 h (Table 1C). Under the reaction conditions, the 0.1 wt% of Cu was most effective and it promoted the synthesis rate by a factor of 2.3 times (Figure 1). One of the plausible explanations is that the positive effects to induce the Ce⁴⁺ site reduction to facilitate H2 dissociation and spillover on the catalyst.
surface and negative effects to block (cover) the surface active sites for DMC synthesis, e.g., the adsorption/activation sites for methanol, compromised to make a synthesis rate maximum at the Cu amount of 0.1 wt%.

The maximal DMC synthesis rate using Cu–CeO2 catalyst (0.1 wt% Cu) at 393 K and 1.3 MPa was 0.95 mmol h⁻¹ gcat⁻¹ (Table 1f), but the rate at 403 K and 6.6 MPa was quite higher (3.1 mmol h⁻¹ gcat⁻¹), nearly equivalent to those in literature using CeO2 (1.8–5.1 mmol h⁻¹ gcat⁻¹) at even severe conditions (403 K and 8.7 MPa) (Yoshida et al., 2006), demonstrating the effects of pre-reduction and/or the Cu addition to CeO2 found in this work. The S_BET values (78–94 m² gcat⁻¹; Table 2) for Cu–CeO2 catalysts (0.1–0.5 wt% Cu) were also similar to those for CeO2 catalyst reported (80 m² gcat⁻¹) (Yoshida et al., 2006).

The effects of ZrO2 mixed with CeO2 (Tomishige et al., 2001; Zhang et al., 2011b) were also interpreted to enhance the redox chemistry between Ce⁴⁺ and Ce³⁺. In this sense, the redox of Cu⁺ and Cu²⁺ may enhance the redox between Ce⁴⁺ and Ce³⁺. We tested Co–CeO2 catalyst under the reaction condition of Table 1d. The conversion of methanol to DMC was 0.23% (not listed), slightly inferior to Cu–CeO2 catalyst. Furthermore, in our preliminary results, the conversions to DMC using Fe–CeO2 and Ni–CeO2 catalysts were nearly equivalent to that using Co–CeO2 catalyst. Thus, the effects of hydrogen activation and/or redox of added metal (Fe, Co, Ni, or Cu) to CeO2 may work in similar way: enhancing effects of mixed metal ions and/or activating effects of hydrogen during pretreatment.

The reactions at lower reaction temperatures were tested (Table 1E). At 2.7 MPa using Cu–CeO2 catalyst (0.5 wt% of Cu), DMC was formed at as low as 353 K (Table 1E). The temperature dependence of DMC synthesis rates nicely followed the Arrhenius equation to give the apparent activation energy: 120 kJ mol⁻¹. This means that the effects of hydrogen activation and/or redox of added metal (Fe, Co, Ni, or Cu) to CeO2 may work in similar way: enhancing effects of mixed metal ions and/or activating effects of hydrogen during pretreatment.

The progress of catalysts to synthesize DMC from CO2 is quite fast, especially under relatively mild conditions (see the Introduction section). The Cu–CeO2 catalysts in this study are one of the good catalysts to work at relatively mild conditions. The dependence of synthesis rates on pressure and temperature (Table 1) was interpreted based on X-ray spectroscopy in next section by monitoring the oxygen defect sites and Ce³⁺.

**ACTIVE SITES OF DMC SYNTHESIS**

The dependence of DMC synthesis on the CO2 pressure (previous section) was proportional (Figure 2). This fact suggested that the key reaction step of DMC synthesis depended linearly on the CO2 concentration.

To provide the insight into the surface reaction mechanism, the electronic state and structure for Ce sites were investigated using Ce L₃-edge XANES. 10–15% of the Ce⁴⁺ sites of as-prepared CeO2 or Cu–CeO2 (0.5 wt% of Cu) were reduced to Ce³⁺ based on the shoulder peak intensity at 5727 eV (Figure 4b,c). Similarly, 10% of the Ce⁴⁺ sites of as-prepared Cu–CeO2 (0.1 wt% of Cu) were reduced to Ce³⁺ under H2 at 673 K, but a half of the Ce³⁺ sites were re-oxidized to Ce⁴⁺ by the introduction of CO2 at 290 K (Figure 4d,e). These changes in the XANES spectra suggested the adsorption of CO2 at the surface defect sites over the catalyst and the associated, neighboring Ce³⁺ sites to the defects were re-oxidized to Ce⁴⁺. This reduction and re-oxidation mechanism was already reported on CeO2 layers grown over Cu(111) surface (Staudt et al., 2010).

The proposed reaction mechanism was shown in Figure 5. Based on the dependence of DMC synthesis rates on the CO2 pressure and the change of a shoulder peak at 5727 eV in the Ce L₃-edge XANES spectra, O vacancy was assumed as defect site and worked to adsorb CO2. The population of O vacancy should increase by the reduction in H2 and/or by the presence of Cu sites in catalysts. In order to synthesize DMC, surface Lewis base sites are required to subtract H atom from methanol (Figure 5). If each H atom was subtracted at the Lewis base site from two methanol molecules, DMC and water molecules are formed to restore an O vacancy site.

**CONCLUSIONS**

Reduction of CeO2 and Cu–promoted CeO2 catalysts in hydrogen at 673 K was effective to enhance the DMC synthesis from CO2 and methanol by a factor of 1.6–1.2 times. Added Cu worked cooperatively with CeO2 catalysts as it accelerated the partial reduction of Ce⁴⁺ sites to Ce³⁺. At the same time, doped Cu sites may block surface active sites. As a compromise, the DMC synthesis rate was maximal: 0.95 mmol h⁻¹ gcat⁻¹ at 393 K and 1.3 MPa (total pressure) in 2 h when the Cu amount was 0.1 wt% for reduced Cu–CeO2 catalyst. The DMC synthesis was possible at the reaction temperature as low as 353 K (2.7 MPa) using the reduced Cu–CeO2 catalyst. The apparent activation energy was calculated to be 120 kJ mol⁻¹. Based on the
Ce L3-edge XANES, 10% of Ce sites were reduced to Ce3+ by the reduction in H2 for Cu–CeO2 (0.1 wt% of Cu) while half of them were re-oxidized to Ce4+ by the introduction of CO2 at 290 K. A linear rate dependence on CO2 pressure and the re-oxidation in CO2 suggest that the adsorption of CO2 might be the key step in DMC synthesis. H subtraction from methanol needs to occur at the neighboring sites of adsorbed CO2. Two methoxy groups and adsorbed CO2 combine then to form DMC and water and restores surface O vacancy (defect site).

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