CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

- Ethanol Anhydrous (99.8 %purity, Carlo Erba)
- Ammonia Solution (25 vol%, Qrec)
- $Ce(NO_3)3 \cdot 6H_2O$ (99.5 %purity, Acros)
- $ZrO(NO_3)_2 \cdot 8H_2O$ (99.5 %purity, Acros)
- Diethyl Carbonate (99 %purity, Acros)
- Diethyl Acetal (98 %purity, Merck)
- Acetaldehyde (98 %purity, Merck)
- Molecular Seive UOP Type 3A (Fluka)
- Liquid Carbon Dioxide (99.99 %purity, Praxair)

3.1.2 Gases

- Carbon Dioxide (99.99 %purity, Praxair)
- Hydrogen (99 %purity, Praxair)
- Nitrogen (99 %purity, Praxair)
- Helium (99 %purity, Praxair)
- Air Zero (99 %purity, Praxair)

3.1.3 Equipment

- 250 mL stainless steel autoclave reactor (Parr Instrument)
- Syringe pumps (Teledyne ISCO, Model 1000D)
- Gas Chromatograph (Agilent 6890N) installed with an FID and equipped with a DB-WAX capillary column
- Gas Chromatograph (LECO Pegasus) connected to a time-of-flight mass spectrometer (4D GC×GC TOFMS)

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- Thermogravimetric and Diffrential Thermal Analyzer (Pyris Diamond TG/DTA, Perkin Elmer Instrument)
- Brunauer-Emmett-Teller (BET) Surface Area Analyzer (Quantachrome Corporation Autosorb-1)
- X-ray Diffractometer (Bruker AXS)
- Temperature Programmed Desorption Apparatus (Thermo Finnigan, modeled TPD/R/O 1100)

3.2 Methodology

3.2.1 Catalyst Preparation

$Ce_xZr_{1-x}O_2$ catalysts where x = 0, 0.07, 0.20, and 0.40 were prepared at room temperature by the co-precipitation using $Ce(NO_3)_3 \cdot 6H_2O$ (99.9%, Acros) and $ZrO(NO_3)_2 \cdot 8H_2O$ (99.9%, Acros) as precursors, and ammonium hydroxide solution as a precipitator. After the desired amounts of the precursors in various ratios were determined according to the procedure provided in Appendix B, the precursors were dissolved in distillated ion-exchanged water. Both solutions were mixed together and adjusted for pH of the solution to 10.2 by using a 5 vol% ammonium hydroxide solution. The precipitates were filtered and calcined at the desired calcination temperature for 3 h. The catalysts were ground into fine powder before use.

The prepared catalysts were divided into 2 types according to the calcination temperature at 700 and 500 °C. In this work, the prepared catalysts consisted of ZrO_2, $Ce_{0.07}Zr_{0.93}O_2$, $Ce_{0.2}Zr_{0.8}O_2$, and $Ce_{0.4}Zr_{0.60}O_2$ are designated to ZrO_2, 7%Ce-Zr, 20%Ce-Zr, and 40%Ce-Zr, respectively.

3.2.2 DEC Synthesis from EtOH and scCO_2

0.5 g of the catalyst was loaded into a 250 mL stainless steel autoclave before it was connected with the experimental system as shown in Figure 3.1. Next, liquid carbon dioxide was used to purge the system prior to begin the experiment for eliminating air. A desired amount of ethanol was loaded into the autoclave using a

syringe pump. Liquid carbon dioxide was filled in a syringe pump at the desired volume at a low volumetric flow rate (1.0 mL/min) to keep it in liquid form and was transferred into the autoclave at the same flow rate. The desired volume of liquid carbon dioxide was calculated from its density at certain pressure and room temperature (25 °C) as provided in Appendix A.

After that, the autoclave was allowed for batch wise operating mode. The system was sealed at a stirring rate of 100 rpm. The reaction temperature and pressure were raised to a desired supercritical condition at a heating rate of 5 °C/min. During the experiment, the liquid sample was taken out every hour for analyzing its composition to evaluate the product quantitatively and qualitatively. After the temperature was reached the desired value, it was held constant for up to 8 h in typical operation or up to 48 h in optional operation.
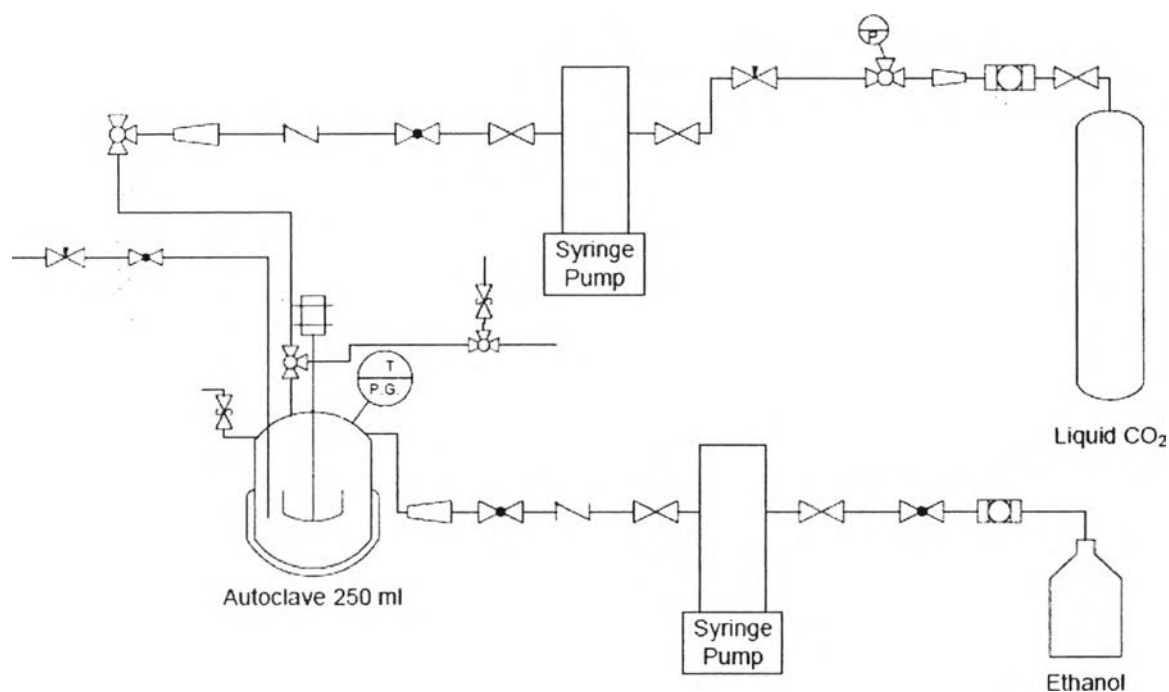

Figure 3.1 Schematic of the DEC synthesis from EtOH and $scCO_2$ experimental system.

Table 3.1 The parameters investigated in DEC synthesis

Parameter	Range
Catalyst	
Ce/Ce+Zr molar ratio	0, 0.07, 0.20, and 0.40
Calcination temperature (°C)	500 and 700
Reaction Conditions	
Reaction temperature (°C)	110, 140, and 170 °C
Feed molar ratio (CO_2:EtOH)	1:1, 1:2, and 1:4
Operation	Supercritical and gas phase
Reaction time (h)	Up to 8 (typical)
	Up to 48 (optional)

3.2.2.1 Liquid Product Analysis

Since diethyl carbonate (DEC), diethyl acetal (DA), and acetaldehyde (AC) were expected to obtain as the resultant products, the calibration curves of the products were determined by using the standards obtained by knowing their accurate concentration in ethanol.

The conversion and the products selectivity were calculated using the following equations:

$$\text{EtOH conversion (\%)} = \frac{100 \times (2 \times \text{moles of DEC} + \text{moles of AC} + 2 \times \text{moles of DA})}{\text{Initial mole of EtOH}} \quad (3.1)$$

$$\text{DEC Selectivity (\%)} = \frac{100 \times (\text{moles of DEC})}{(\text{moles of DEC} + \text{moles of AC} + \text{moles of DA})} \quad (3.2)$$

In this research work, the liquid products were analyzed using a gas chromatograph (Agilent 6890N) installed with an FID and equipped with a DB-WAX capillary column. 1 μL of liquid sample was injected into the column through

a septum after the GC was conditioned in accordance with the desired operating conditions. The GC operating conditions are summarized as shown in Table 3.2.

Table 3.2 Parameters for the GC operation

Parameter	Value
Oven	
Set point (°C)	40
Initial temperature (°C)	40
Ramping rate (°C/min)	10
Hold time (min)	5
Final temperature (°C)	150
Inlet	
Mode	Split
Split ratio	200
Gas	Helium
Detector	
Temperature (°C)	300
H_2 flow rate(mL/min)	35
Air zero flow rate(mL/min)	350
Make up N_2 flow rate(mL/min)	30

3.2.4 Catalyst Characterizations

Thermogravimetric and differential thermal analyses (TG-DTA) were preceded using a Pyris Diamond TG/DTA (Perkin Elmer Instrument). The chamber inside the analyzer was exposed to a continuous flow of the oxygen flow rate (30 mL/min). 0.0827 g of the sample was heated up from 25 to 950 °C at heating rate of 5 °C/min. The mass changes were monitored during temperature increase and TGA and DTA profile were recorded by the TA instrumental thermal analyst system.

BET surface areas of the catalyst were measured by Brunauer-Emmett-Teller (BET) method with N_2 adsorption at 77 K (seven point BET method

using a Quantachrome Corporation Autosorb-1). Prior to the measurements, 0.5 g of the sample was outgassed to eliminate volatile components on the surface at 250 °C for overnight. By measuring the quantity of N_2 adsorbed onto or desorbed from a solid surface at 7 equilibrium vapor pressure (P/P_o) value (0.05, 0.075, 0.10, 0.15, 0.20, 0.25, and 0.30) by the static volumetric method, the data were obtained by admitting or removing N_2 into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for N_2.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation.

$$1/[W \times (P_o/P)\text{-}1] = 1/[W_m \times C] + [(C\text{-}1)/(W_m \times C)] \times (P/P_o) \tag{3.3}$$

where W = weight of N_2 adsorbed at relative pressure P_o;

W_m = weight of adsorbate constituting a monolayer of surface coverage;

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$\text{Surface area of sample} = W_m \times A_{nitrogen} \times (6.02 \times 1023)/M_{w, nitrogen} \tag{3.4}$$

where $A_{nitrogen}$ = Cross-sectional area of one molecule nitrogen (0.162 nm^2 at 77 K);

$M_{w, nitrogen}$ = molecular weight of nitrogen (28).

Crystalline phases of the catalysts were analyzed using an X-ray diffractometer (a Bruker AXS X-ray diffractometer model D8 advanced with wide angle using Cu radiation and a power of 40 kV × 30 mA). The intensity data were collected at 25 °C over a 2θ range of 10-80° with a scan speed of 1° (2θ)/min and a scan step of 0.02° (2θ).

The XRD patterns were used for the average crystalline size from the broadening of a diffraction line at half the line maximum intensity in Equation 3.5 called Bragg's equation.

$$L_{hkl} = (0.89 \times \lambda)/(\beta_{hkl} \times \cos\square) \tag{3.5}$$

where L_{hkl} = crystal size (nm);

  λ = X-ray wavelength (0.51418 nm obtained from the equipment);

  β_{hkl} = broadening of the diffraction line measured at half the line maximum intensity (rad);

  $\square$ = diffraction angle (rad).

Acid and basic properties of the catalysts were determined by temperature-programmed desorption (TPD) of NH_3 and CO_2, respectively, using a Thermo Finnigan, modeled TPD/R/O 1100. In pretreatment step, about 0.2 g of the sample was placed in a quartz tube, pretreated at 473 K in a nitrogen flow rate at 20 mL/min for 30 min to eliminate moisture, and saturated with pure NH_3 or CO_2 flow rate at 20 mL/min for 60 min after cooling to 323 K. In analysis step, a helium flow rate of 20 mL/min was purged on the sample to remove physisorbed NH_3 or CO_2 at a heating rate of 10 K/min from 323 to 1173 K hold for 3 h. The desorbed gas (NH_3 or CO_2) from the sample was monitored as a function of temperature and detected with a thermal conductivity detector (TCD).