

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterizations

4.1.1 BET Surface Area Analysis

From Table 4.1, the BET surface area of the catalysts calcined at 700 °C was ranged from ca. 30 to ca. 67 m²/g. The 20%Ce-Zr catalyst yields the highest specific surface area of 67.37 m²/g. The specific surface area was increased with increasing Ce amount. However, too much Ce content caused a decrease in surface area as for the 40%Ce-Zr catalyst.

For the various ratios part, the increasing of BET surface areas in the catalysts from ZrO₂ to 20%Ce-Zr was because the contribution of ceria and zirconia. The addition of ceria in zirconia can enhance the thermal stability of the catalyst (Thammachart *et al.*, 2000).

For the explanation for the reduction of the BET surface area in the higher amount of ceria in the 40%Ce-Zr catalyst, XRD patterns in Figure 4.1 was needed to be used. The XRD pattern of the 40%Ce-Zr catalyst showed no ZrO₂ tetragonal or monoclinic phase compared to ZrO₂ to the 20%Ce-Zr catalyst. However, the similarity in the XRD pattern of the 40%Ce-Zr catalyst and CeO₂ showed almost the same pattern at 28, 33, 48, 58, and 60 2 θ (degree). It was indicated that ceria amount in the 40%Ce-Zr catalyst was in the cubic phase of CeO₂ rather than tetragonal phase of ZrO₂. Due to the cubic phase of CeO₂ which has the particle form in needle shape and resulted to a small active surface area (Thammachart *et al.*, 2000), the 40%Ce-Zr catalyst dominated by the cubic phase of CeO₂ has the BET surface area less than the BET surface area in the 20%Ce-Zr catalyst.

It is apparent that increasing calcination temperature from 500 to 700 °C resulted in decreasing surface area from ca. 73 to ca. 51 m²/g for the 7%Ce-Zr catalyst due to the sintering.

Table 4.1 BET surface areas of the prepared CeO₂-ZrO₂ catalysts calcined at 500 and 700 °C for 3 h

Catalyst	BET surface area (m ² /g)
ZrO ₂ at 700 °C	29.60
7%Ce-Zr at 700 °C	50.99
20%Ce-Zr at 700 °C	67.37
40%Ce-Zr at 700 °C	36.52
7%Ce-Zr at 500 °C	72.63

4.1.2 X-ray Diffraction (XRD)

Figure 4.1 shows XRD patterns of the CeO₂-ZrO₂ catalysts with various ratios (0, 7, 20, 40, and 100%Ce-Zr) calcined at 700 °C. The crystalline structure of the CeO₂-ZrO₂ catalyst was transformed from monoclinic ZrO₂ phase to tetragonal ZrO₂ phase when adding CeO₂ from 7 to 20% and the cubic form of CeO₂ was dominated at the 40%Ce-Zr catalyst noticed by the peak shifted from the ZrO₂ pattern to CeO₂ pattern (Nakatani and Okamoto, 2003). The diffraction peaks are shifted to lower degrees with increasing ceria amount. Table 4.2 presents the crystal sizes and crystal phases of the catalyst (E. Diaz *et al.*, 2006). Crystal sizes of the catalysts except for ZrO₂ and CeO₂ were decreased with Ce addition.

The diffraction peaks are shifted to lower degrees with an increasing of the ceria amount. This observation indicates a shrinkage of the lattice due to the replacement of Ce⁴⁺ with Zr⁴⁺, which coincides with the fact that the cation radius of Zr⁴⁺ (0.86 Å) is lower than that of Ce⁴⁺ (1.09 Å) (Thammachart *et al.*, 2000).

The XRD pattern of the 40%Ce-Zr catalyst was slightly different from the others. From the observation, the peaks of the 40%Ce-Zr catalyst were broadened to the peaks of CeO₂. The result indicates that the high amount of ceria can cause the domination of the cubic phases of CeO₂ over the surface of the 40%Ce-Zr catalyst. This phenomenon also occurred as reported by Nakatani and Okamoto in 2003.

Figure 4.2 shows XRD patterns of the 7%Ce-Zr catalysts at different calcination temperatures. The results showed a slight change in the intensity without

changing phase with calcination temperature. The different intensities of the peaks may originate from the different degrees of porosity and crystalline of ceria-zirconia (Thammachart *et al.*, 2000)

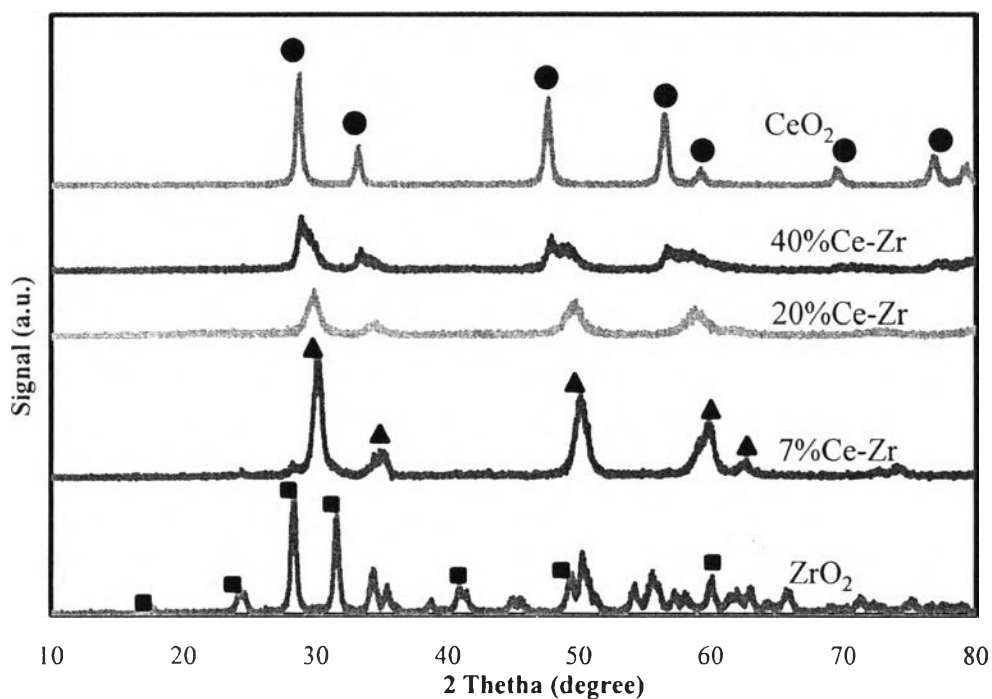


Figure 4.1 XRD patterns of $\text{CeO}_2\text{-ZrO}_2$ catalysts with various ratios (0, 7, 20, 40, and 100 %Ce-Zr) calcined at 700 °C (Monoclinic phase of ZrO_2 (■), tetragonal phase of ZrO_2 (▲), and cubic phase of CeO_2 (●)).

Table 4.2 Summary of the crystal size and phase of the catalyst (E. Diaz *et al.*, 2006)

Catalyst ^a	Crystal size ^b (nm)	Crystal Phase
ZrO ₂	17.07	Monoclinic of ZrO ₂
7%Ce-Zr	10.83	Tetragonal of ZrO ₂
20%Ce-Zr	7.29	Tetragonal of ZrO ₂
40%Ce-Zr	6.05	Cubic of CeO ₂ (trace of tetragonal ZrO ₂)
CeO ₂	16.07	Cubic of CeO ₂
7%Ce-Zr calcined at 500 °C	10.45	Tetragonal of ZrO ₂

^a Calcined at 700 °C

^b Determined by Bragg's equation in Chapter III

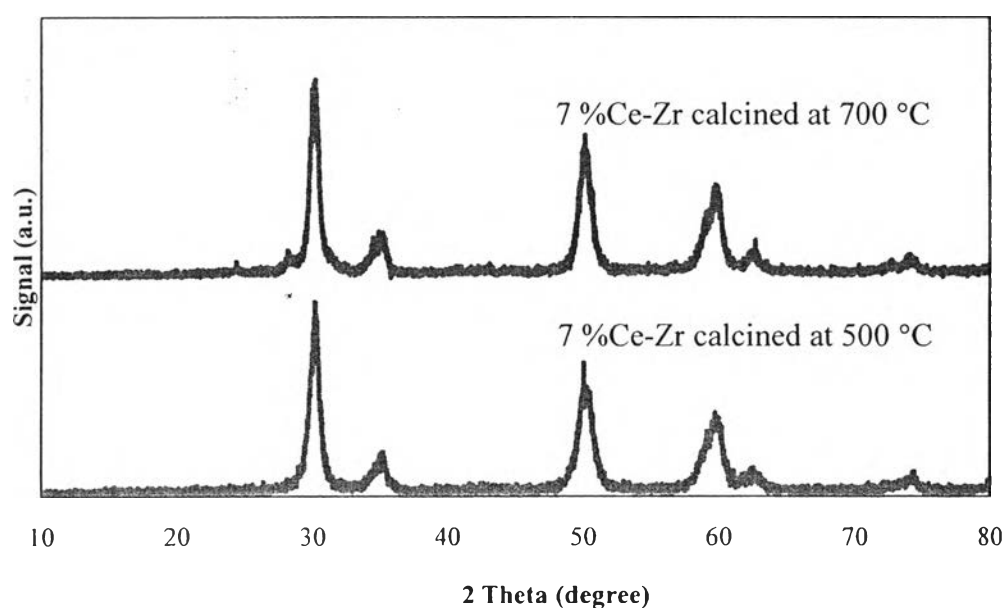


Figure 4.2 XRD patterns of the 7%Ce-Zr catalysts at different calcination temperatures.

4.1.3 Thermogravimetric and Differential Thermal Analysis (TG-DTA)

In Figure 4.3, from DTG profile, 3 step of decomposition were identified to be the loss of adsorbed water around 100 °C, water inside pores at ca. 200 °C, and the decomposition of metal nitrates at ca. 400 °C. From TG profile, the weight loss of the catalyst was stable at 86% when the temperature was increased more than 500 °C. This suggests that the catalysts should be calcined at the temperature higher than 500 °C to decompose all contaminants.

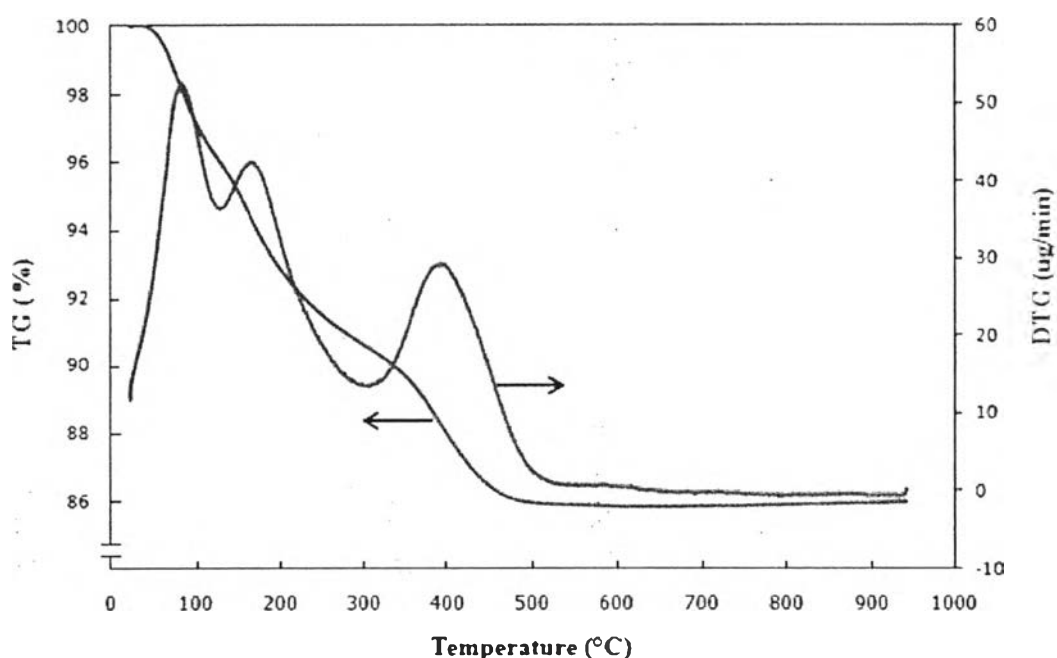


Figure 4.3 TG-DTG profiles of 20%Ce-Zr catalyst (Heating rate 5 °C/min, Pt basket N₂ flow rate (30 mL/min), and sample weight 8.727 mg).

4.1.4 Temperature Programmed Desorption (TPD) of NH₃ and CO₂

Figures 4.4 and 4.5 show NH₃-TPD and CO₂-TPD profiles of the catalysts with various ratios (0, 7, 20, and 40%Ce-Zr) at calcination temperature of 700 °C, respectively. Figures 4.6 and 4.7 show NH₃-TPD and CO₂-TPD profiles of the 7%Ce-Zr catalysts at different calcination temperatures. The peak position indicates the acid-base strength of the surface sites of the catalysts (E. Diaz *et al.*, 2006).

In Figure 4.4, the pattern of ZrO_2 showed a major peak at 530 °C. After adding ceria amount from 7 to 40%Ce-Zr, the major peak of each catalyst was shifted to low temperature. The major peak of the 7 and 20%Ce-Zr catalysts located at 460 °C with an extra peak of 20%Ce-Zr at 680 °C. The difference between 7%Ce-Zr and 20%Ce-Zr was the high acid density in 20%Ce-Zr. Finally, the major peak 40%Ce-Zr showed at 330 °C.

In Figure 4.5, the pattern of ZrO_2 showed a peak at 130 °C. After adding ceria amount from 7 to 40%Ce-Zr, the major peak of each catalyst at high temperature was not detected. The major peak of 7%Ce-Zr and 20%Ce-Zr located at 160 °C with a small peak of 20%Ce-Zr at 460 °C. The difference between 7%Ce-Zr and 20%Ce-Zr was the high basic density in 20%Ce-Zr. Finally, the major peak 40%Ce-Zr showed two small peaks at 120 and 300 °C.

Decreasing in acid strength of the ceria-zirconia catalysts occurs because ceria has base strength higher than zirconia and base strength in the catalysts was increased due to the Ce addition as well (M.E. Brown and P.K. Gallagher, 2008).

In Figure 4.6, the peak of TPD- NH_3 pattern of 7%Ce-Zr calcined at 500 °C was located at 500 °C which was higher than the peak of 7%Ce-Zr calcine at 700 °C. In Figure 4.7, the peak of TPD- CO_2 pattern of 7%Ce-Zr calcined at 500 °C was located at 130 °C which was lower than the peak of 7%Ce-Zr calcine at 700 °C. The result shows that the catalyst at low calcination temperature has more roughness, and higher calcination temperature makes the surface more plain. The roughness sites have more coordination unsaturated cations and anions which bring to higher acidity and basicity (W. Wang *et al.*, 2009).

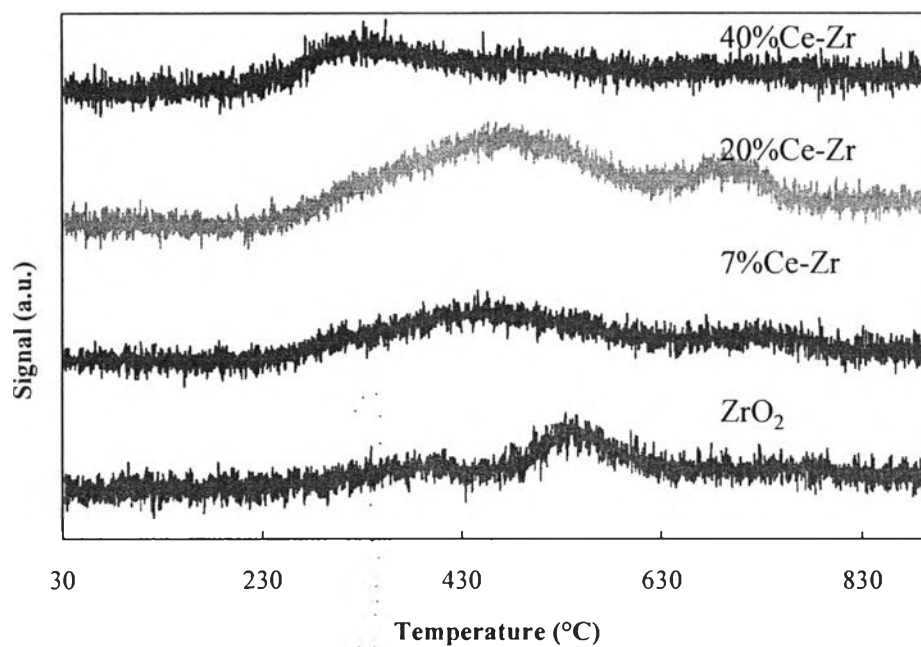


Figure 4.4 NH₃-TPD profiles of the CeO₂-ZrO₂ catalysts with various ratios (0, 7, 20, and 40 %Ce-Zr) calcined at 700 °C.

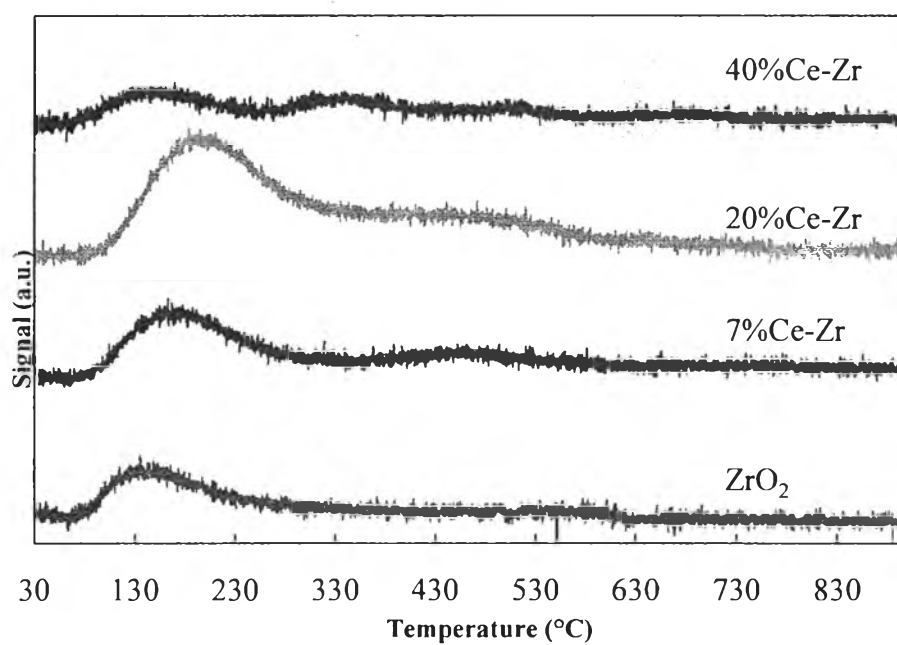


Figure 4.5 CO₂-TPD profiles of the CeO₂-ZrO₂ catalysts with various ratios (0, 7, 20, and 40 %Ce-Zr) calcined at 700 °C.

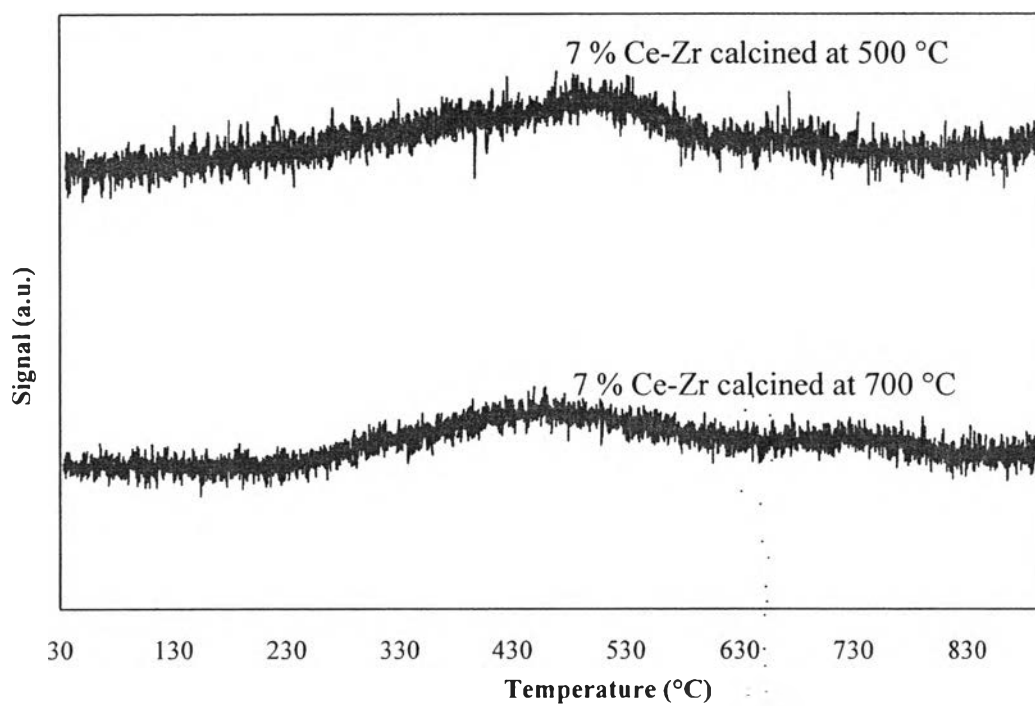


Figure 4.6 NH₃-TPD profiles of 7 %Ce-Zr at different calcination temperatures.

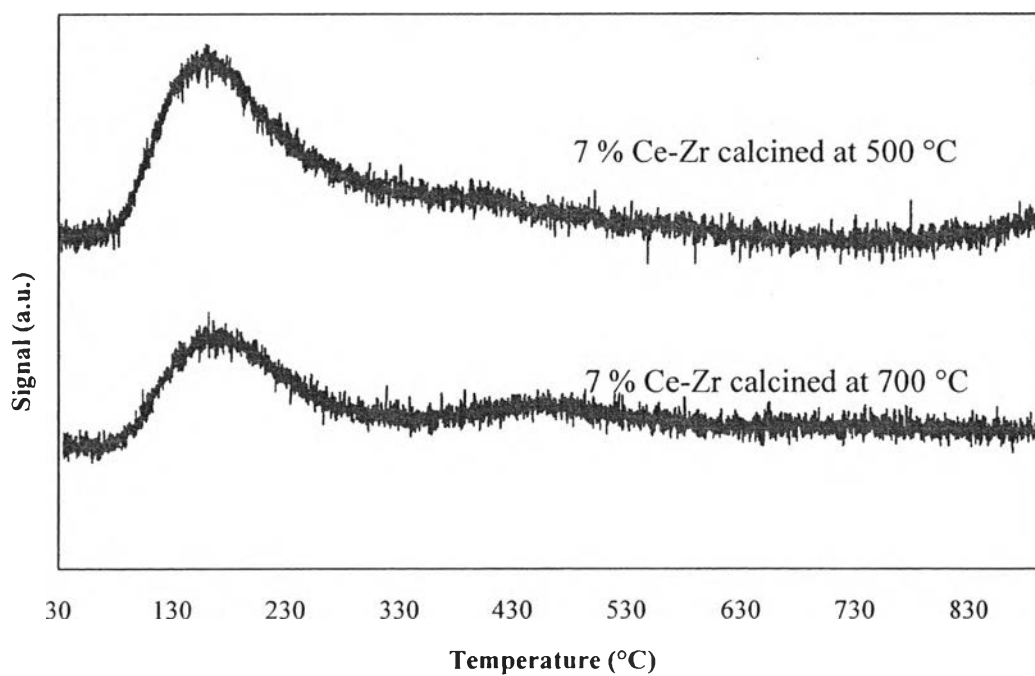


Figure 4.7 CO₂-TPD profiles of 7 %Ce-Zr at different calcination temperatures.

4.2 DEC Synthesis

To confirm that diethyl carbonate is synthesized in the experiment, the sample was analyzed by the GC×GC TOFMS to determine mass spectra of diethyl carbonate. Figure 4.8 shows the mass spectra of diethyl carbonate synthesized from ethanol and supercritical carbon dioxide over the 20%Ce-Zr catalyst calcined at 700 °C. In Figure 4.8, the peaks in the mass spectra of diethyl carbonate at 91 and 63 m/z are C₃H₇O₃ and CH₃O₃, respectively (P. Brown and C. Djerassi, 1966). The result proved that diethyl carbonate can be synthesized in supercritical condition.

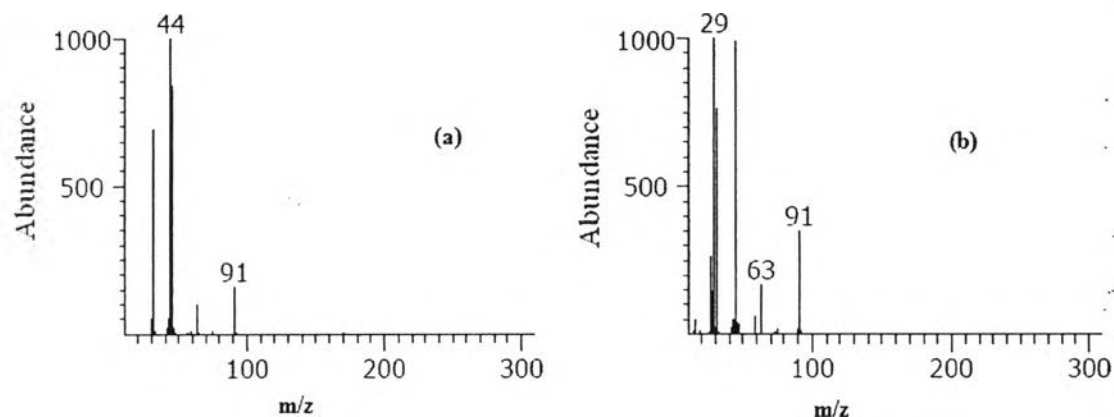
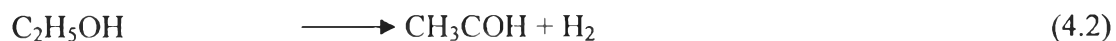


Figure 4.8 Mass spectra of diethyl carbonate in DEC synthesis from the sample (a) and from the database (b). Reaction conditions: EtOH:CO₂ = 1:1 mole, reaction temperature 140 °C, reaction time 8 h, 0.5 g of the 20%Ce-Zr catalyst calcined at 700 °C, obtained using the GC×GC TOFMS.

The other by-products in this work were diethyl acetal and acetaldehyde. Equations 4.1 to 4.3 represent the possible chemical reactions of diethyl carbonate, acetaldehyde, and diethyl acetal, respectively.



4.2.1 Effect of the CeO₂-ZrO₂ Catalysts

The amount of DEC produced over various CeO₂-ZrO₂ catalysts calcined at 700 °C at 140 °C and 1300 psig in a period of 8 h is shown in Figure 4.9. The results show that the amount of DEC was increased at different rates for which its initial production rate was raised in the following order: 7%Ce-Zr > 40%Ce-Zr > 20%Ce-Zr > ZrO₂. However, at the end of 8 h, the 20%Ce-Zr catalyst yielded higher DEC amount than the 40%Ce-Zr. Table 4.3 provides the DEC amount and selectivity over various catalysts at a reaction time of 8 h. The 7%Ce-Zr catalyst gave the highest DEC amount and selectivity. This was attributed to the catalyst phase and acid-base properties (Wang *et al.*, 2009). The presence of tetragonal phase of ZrO₂ by incorporating a certain amount of Ce along with weak acid-base properties was essential for the synthesis of DEC. As observed in Tables 4.1 and 4.3, since the 7%Ce-Zr catalyst calcined at 700 °C which did not possess the maximum specific surface area yielded the highest DEC amount and selectivity, the 7%Ce-Zr catalyst calcined at 500 °C having the maximum specific surface area was tested for its performance under the same operating conditions.

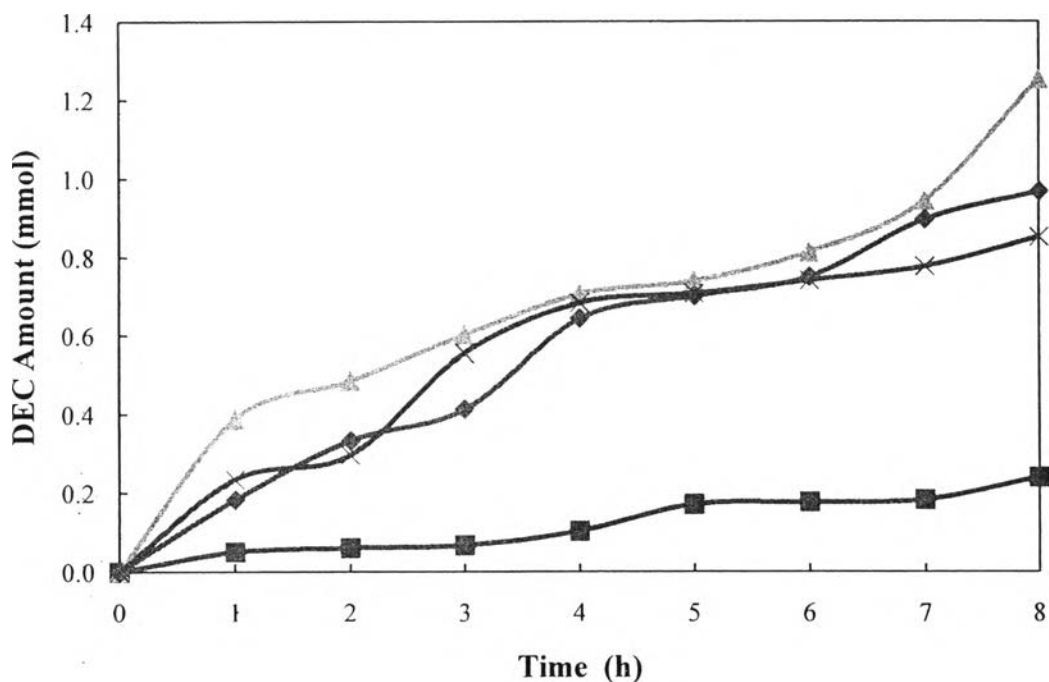


Figure 4.9 Effect of the CeO₂-ZrO₂ catalysts calcined at 700 °C (ZrO₂(■), 7%Ce-Zr(▲), 20%Ce-Zr(◆), and 40%Ce-Zr(×)) on the amount of DEC produced. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, pressure 1300 psig, reaction time 8 h, 0.5 g of the CeO₂-ZrO₂ catalysts.

Table 4.3 DEC amounts and selectivities attained at 8 h reaction time over various catalysts calcined at 700 °C. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, pressure 1300 psig, reaction time 8 h, 0.5 g of the catalysts.

Catalyst	DEC amount (mmol)	DEC selectivity (%)
ZrO ₂	0.24	53.95
7%Ce-Zr	1.25	97.55
20%Ce-Zr	0.97	85.70
40%Ce-Zr	0.85	81.51

4.2.2 Effect of Calcination Temperature

From Figure 4.10, it can be seen that the catalyst calcined at 700 °C gave higher DEC amount but lower BET surface area than calcined at 500 °C. This might be because the catalyst calcined at 700 °C possessed less acidity and basicity than the catalyst calcined at 500 °C as observed in Figures 4.6 and 4.7.

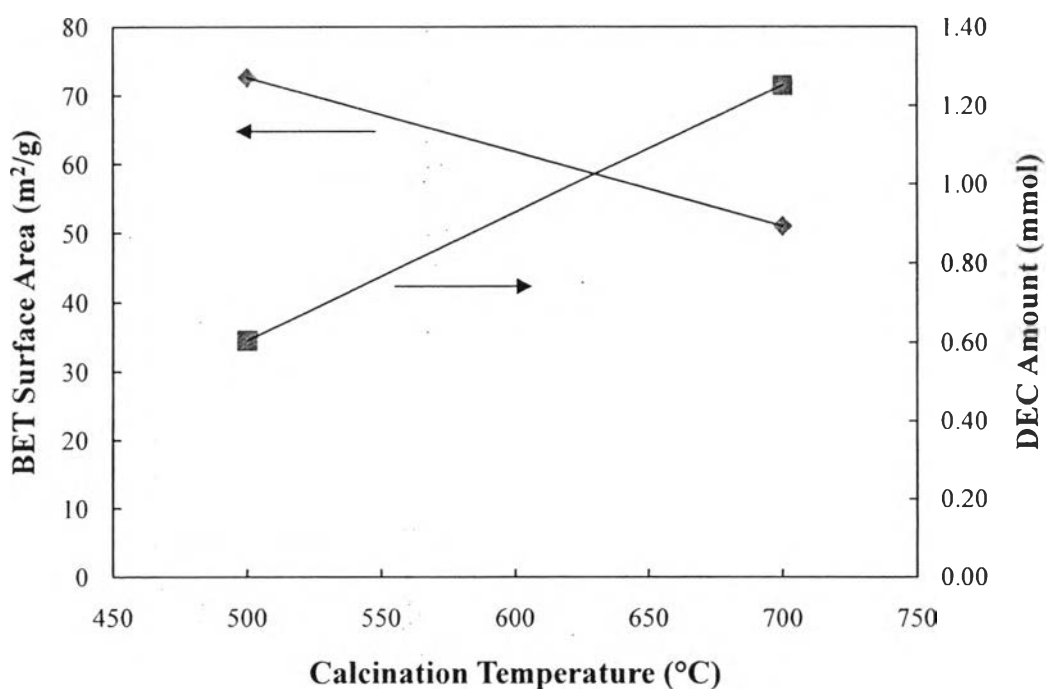


Figure 4.10 Effect of calcination temperature on the DEC amount and BET surface area for the 7 %Ce-Zr catalysts. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, pressure 1300 psig, reaction time 8 h, 0.5 g of the catalysts.

After the catalyst and calcination temperature effects were studied the 7%Ce-Zr calcined at 700 °C was observed to be most active at particular reaction conditions. Therefore, it was selected for further studies on other reaction condition effects.

4.2.3 Effect of Reaction Temperature

In this work, the reaction temperature was varied at 110, 140, and 170 °C based on a pressure limitation of the experimental system and safety concerns. According to the results obtained from Figure 4.11, the optimum reaction temperature in the range of 110 to 170 °C was 140 °C. The negative effect on the catalytic activity at a high temperature was due to the nature of exothermic reaction for DEC synthesis (Wang *et al.*, 2009).

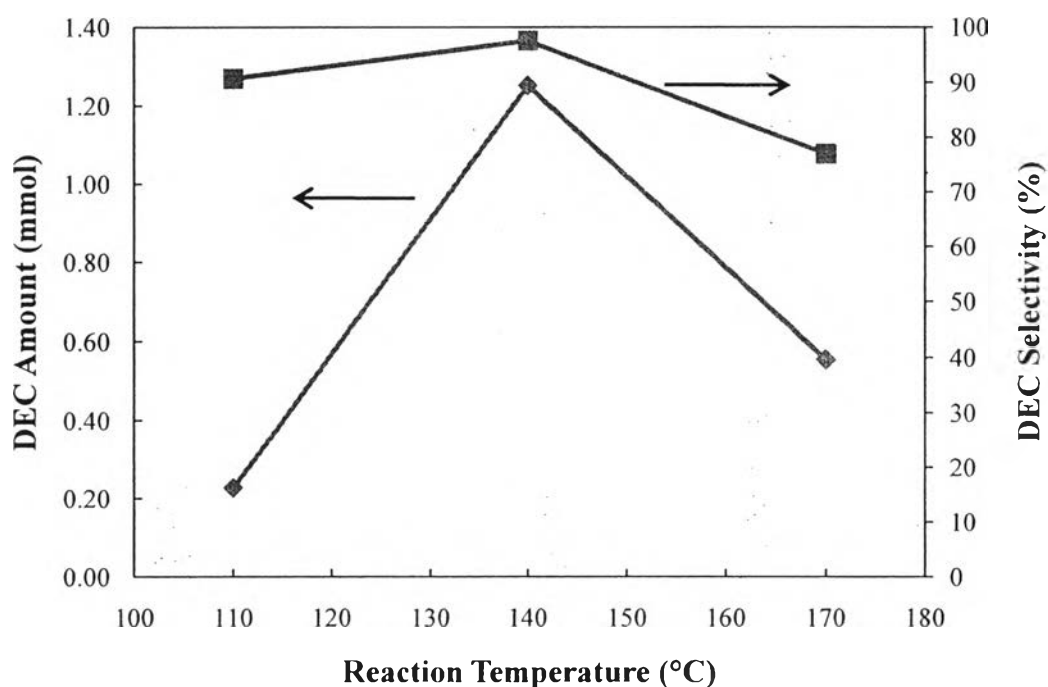


Figure 4.11 Effect of reaction temperature on the DEC production and selectivity for the 7 %Ce-Zr catalyst calcined at 700 °C. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction time 8 h, 0.5 g of the catalyst.

4.2.4 Effect of Molecular Sieve

Because water is a by-product which occurred concurrently with DEC in the equilibrium reaction, water removal can accelerate the forward reaction. In this research work, the comparison of using molecular sieve 3A in external system and internal system was obtained.

Figure 4.12 shows the effect of molecular sieve 3A in external and internal systems on the DEC production for the 7%Ce-Zr catalyst calcined at 700 °C. The trend of DEC production when using molecular sieve 3A in the external system was moderately higher than that in the internal system.

A less quantity of DEC in the internal system may be from the molecule size of CO₂ (2.32 nm, http://en.wikipedia.org/wiki/Carbon_dioxide) is smaller than pore size of the molecular sieve. When the reaction occurred in liquid phase, CO₂ may be replaced in the pore of molecular sieve instead of water.

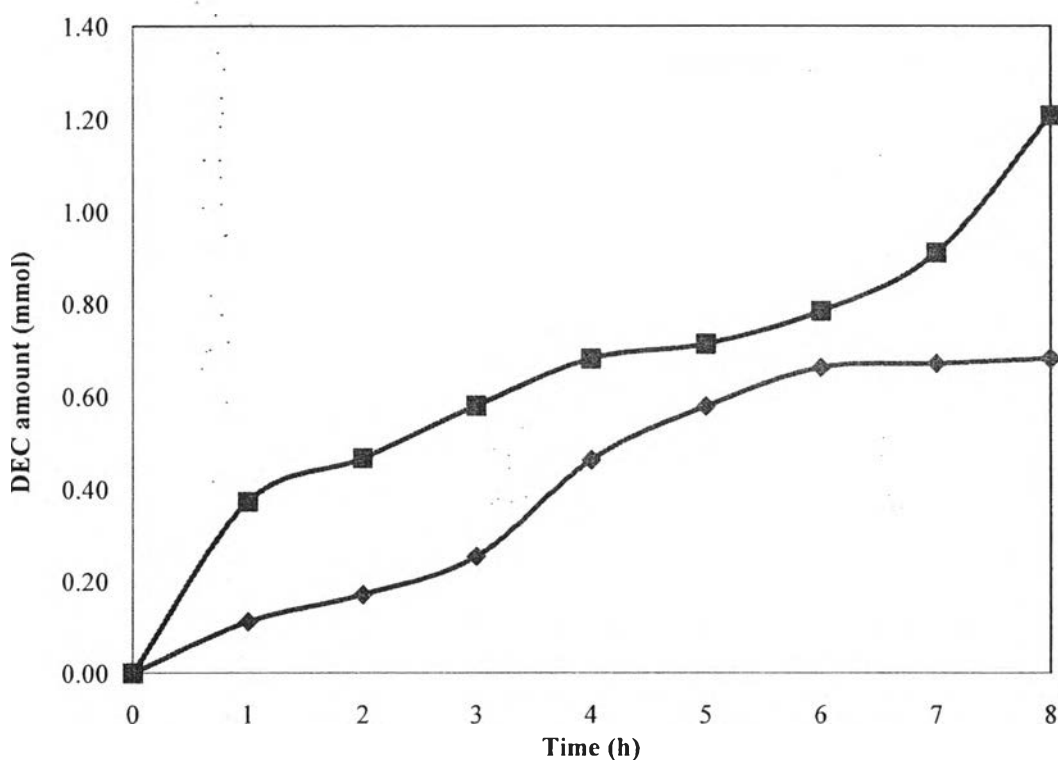


Figure 4.12 Effect of using molecular sieve 3A (external system (■), and internal system (◆)) on the DEC production for the 7 %Ce-Zr catalyst calcined at 700 °C. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, pressure 1300 psig, reaction time 8 h, 0.5 g of the catalysts.

4.2.5 Effect of CO₂:EtOH Feed Molar Ratios

To increase the DEC production, the effect of CO₂:EtOH feed molar ratios was studied by varying its ratios at 1:1, 2:1, and 4:1. The DEC production and selectivity results at various ratios as shown in Figure 4.13 demonstrate that increasing the feed molar ratio can improve the production from 1.25 to 6.04 mmol. Whereas, the selectivity was declined from ca. 97 to ca. 86%.

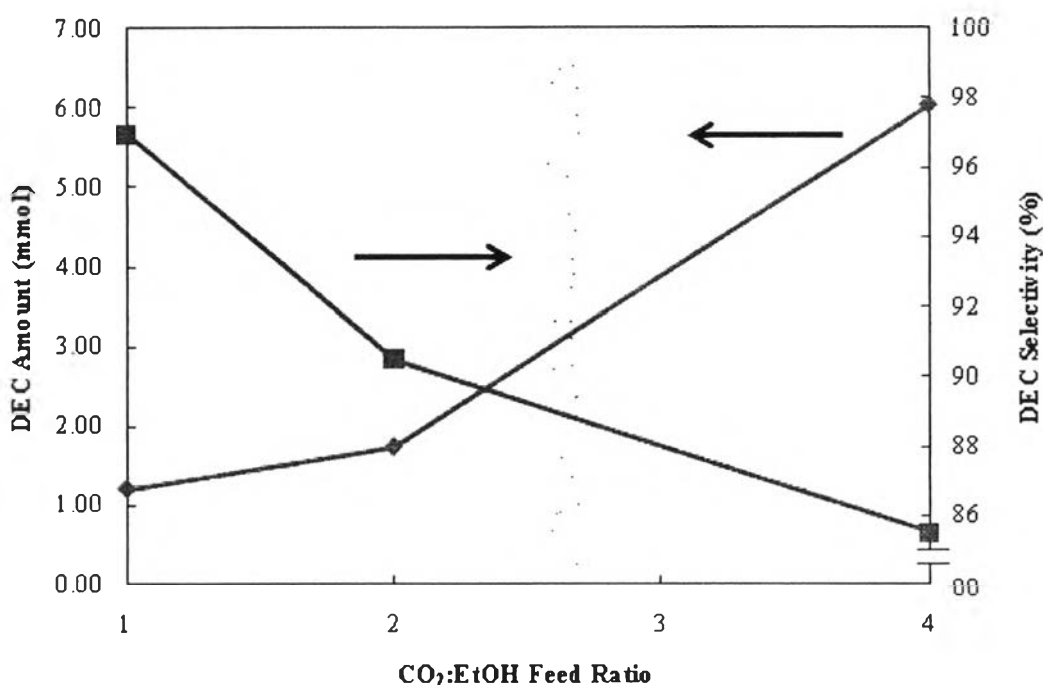


Figure 4.13 Effect of CO₂:EtOH feed molar ratio on the DEC production and selectivity for the 7 %Ce-Zr catalyst calcined at 700 °C. Reaction conditions: reaction temperature 140 °C, reaction time 8 h, 0.5 g of the catalysts.

The reason for the increasing of DEC production may occur because ethanol was diluted more when increasing the feed molar ratio. With this dilution, CO₂ may have a potential to absorb over the catalyst more and reacts with absorbed ethanol which can increase the catalytic reaction. For the negative effect on the DEC selectivity, when CO₂ can absorb over the catalyst more, ethanol which was diluted and not absorbed over the catalyst may react without CO₂ participated in the reaction. Therefore, the side reactions were occurred more when increasing in the feed molar ratio.

4.2.6 Effect of Supercritical and Gas Phase Conditions

To assure that the supercritical condition is an effective way to synthesize DEC rather than the gas phase condition, CO₂ was introduced in the reactor as gas phase in the experiments. The amount of CO₂ gas was calculated based on the density related with temperature and pressure on P-H diagram in appendix A.

DEC production in supercritical and gas phase conditions as shown in Figure 4.14 shows that the amount of DEC which was synthesized from the former condition was higher than the amount of DEC which was synthesized from the latter.

It is apparent that DEC amount can be synthesized in supercritical condition greater than that in gas phase condition. This is because supercritical condition can eliminate the mass transport limitation which can enhance the heterogeneous catalytic reaction (Baiker, 1999).

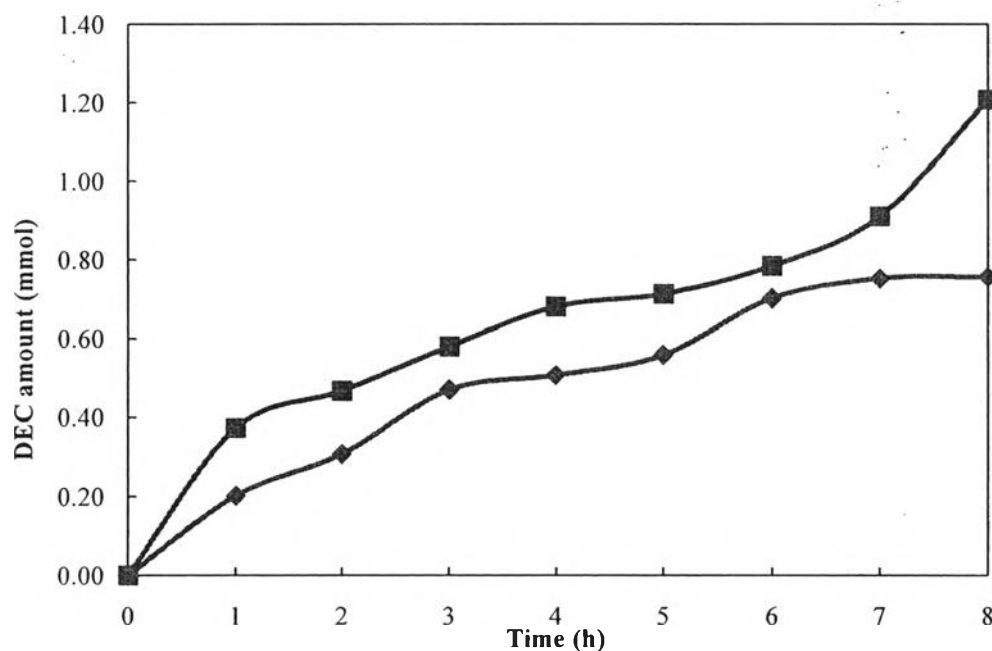


Figure 4.14 Effect of supercritical and gas phase conditions on the DEC production for the 7 %Ce-Zr catalyst calcined at 700 °C in supercritical (■) and gas phase (◆) conditions (1300 and 900 psig, respectively). Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, reaction time 8 h, 0.5 g of the catalysts.

4.2.7 Effect of Reaction Time

To study the maximum amount of DEC produced as a function of time, the reaction time was studied up to 48 hours. Figure 4.14 shows the DEC production with respect to time over the 7%Ce-Zr catalyst at the reaction temperature of 140 °C. It shows that the DEC amount was generated dynamically from 0 to 15 h at 1.35 mmol. After the reaction time of 15 h, the amount of DEC was level off until the reaction time reach at 48 h.

The reason that the DEC production was remained the same after the reaction time at 15 h is because the reaction of DEC from ETOH and CO₂ is controlled by the thermodynamics.

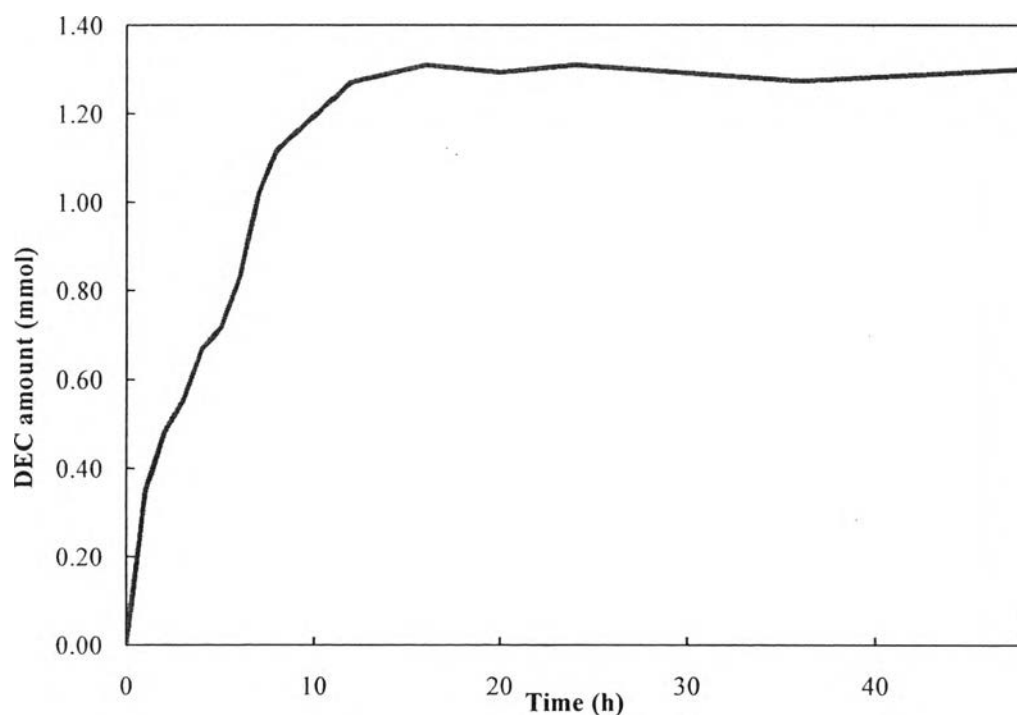


Figure 4.15 Effect of time on the DEC production for the 7 %Ce-Zr catalyst calcined at 700 °C. Reaction conditions: CO₂:EtOH molar ratio = 1:1, reaction temperature 140 °C, 0.5 g of the catalyst.

4.2.8 Comparison between Experimental Results and Equilibrium

Calculations

To compare the resultant DEC in the experiments, equilibrium calculations on the multiple reactions in supercritical phase were performed with the assumption as ideal solution. The detail calculations are given in Appendix C. Figure 4.16 shows the comparison between the amount of DEC obtained from the experiments and the amount of DEC obtained from the equilibrium calculations.

For the experiments at 8 h, DEC was reached the maximum amount (1.25 mmol) at 140 °C. However, the amount of DEC was declined from 110 °C to 170 °C (3.50 to 1.50 mmol) as obtained by the equilibrium calculations.

Due to the exothermic reaction of DEC synthesis from EtOH and CO₂, increasing the reaction temperature would reduce the amount of DEC in theory. However, the trend was different for the experiments due probably to the catalysis dominating the thermodynamic limitation.

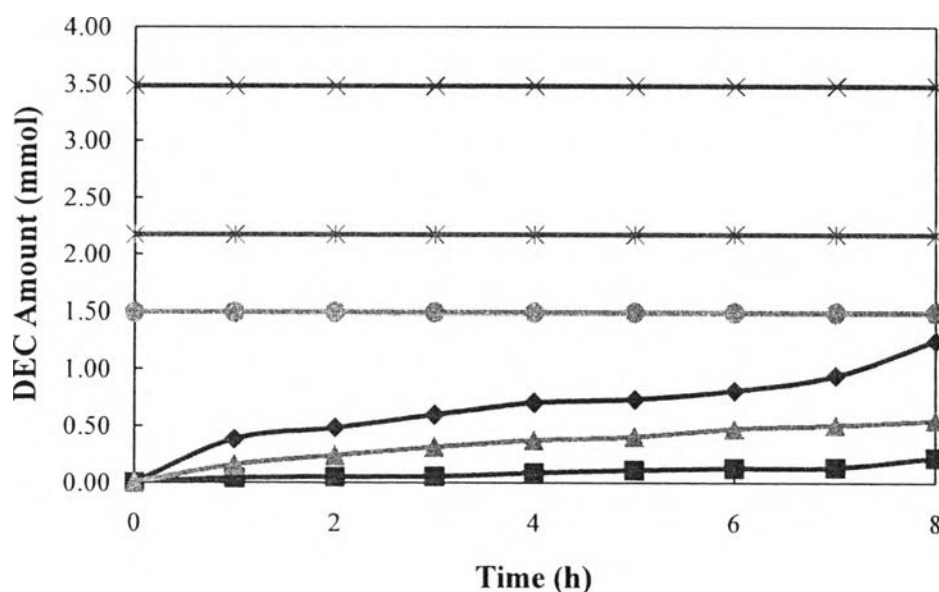


Figure 4.16 The comparison between the amount of DEC from the experiment results of reaction temperature in Figure 4.11 with 110 °C (■), 140 °C (◆), and 170 °C (▲), and the amount of DEC from hand's calculation in the same reaction temperature with 110 °C (×), 140 °C (*), and 170 °C (●).