

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Characterization of Fresh Catalyst

This research studied the catalytic activity of CaO–ZnO as a heterogeneous basic catalyst for biodiesel production via transesterification reaction in a batch reactor. In order to investigate the optimum conditions for this reaction, the catalyst was varied with many parameters, such as amount of Ca loading on ZnO support, calcination temperature, and type of catalyst preparation on the biodiesel yield. Moreover, type of precipitant and precursor concentration in catalyst preparation were studied. In order to explain the catalytic activity of the prepared catalysts, the fresh and spent catalysts were characterized by several techniques, such as XRD, SEM, TPD-CO₂, FTIR, TPR, XRF, surface area analysis, and titration method.

4.1.1 X-ray Diffraction (XRD)

The XRD patterns of ZnO support and CaO–ZnO catalysts for both prepared by co-precipitation (CP) and incipient-wetness impregnation (IWI) methods are shown in Figures 4.1, 4.2 and 4.3. The intensities of diffraction peaks at 31.76°, 34.42°, 36.25°, 47.50°, 56.50°, 62.76°, 66.33°, 67.83°, 68.99°, 72.50°, and 76.91° represented the characteristic crystallinity of ZnO substance (Taufiq-Yap *et al.*, 2011). However, the intensities of diffraction peaks at 32.37°, 37.62°, 53.99°, 64.37°, and 67.49° represented the characteristic crystallinity of CaO substance (Ngamcharussrivichai *et al.*, 2008) for catalysts prepared by IWI method, while the intensities of Ca(OH)₂ diffraction peaks at 18.1°, 28.8°, 34.1°, 47.1°, and 50.8° were observed for catalysts prepared by CP method (Watcharathamrongkul *et al.*, 2010).

For the effect of Ca:Zn atomic ratio of CaO-ZnO catalysts can be explained by the XRD patterns, as shown in Figure 4.1. The XRD patterns of CaO-ZnO catalysts prepared by CP method are shown in Figure 4.1a, the peaks of Ca(OH)₂ and the sharpness peaks of ZnO were observed. An increasing of Ca content or Ca:Zn atomic ratio from 1:5 to 3:1, the XRD diffraction peaks of Ca(OH)₂

particle became higher. This means the Ca(OH)_2 crystallite size became larger at high Ca contents.

The CaO-ZnO catalysts prepared by IWI method (Figure 4.1b) show the sharpness peaks of both CaO and ZnO particles, indicating that the crystallite structure of CaO and ZnO particles might be formed as a cluster or larger size in all of Ca:Zn atomic ratios. The XRD diffraction peaks of CaO particle became higher when increasing the Ca amounts of catalysts. However, the XRD diffraction peaks of ZnO particle became lower. So, the CaO crystallite size could become larger cluster or larger size at high Ca contents.

As mentioned above, it should be noted that the Ca phase of CaO-ZnO catalysts strongly depended on the catalyst preparation. This should be reasonable that why the catalytic activity of CaO-ZnO catalysts with different preparation methods are not the same.

For the effect of calcination temperature is illustrated in Figure 4.2a) (CP) and b) (IWI), the XRD intensities of ZnO and Ca(OH)_2 of CaO-ZnO prepared by CP method became higher after increasing the calcination temperature from 800 °C to 1,000 °C. It can be concluded that at calcination temperature of 800 °C is high enough to change CaCO_3 form to Ca(OH)_2 form. While, the XRD peaks of ZnO and CaO of the CaO-ZnO catalysts prepared by IWI method (Figure 4.2b) exhibited low intensities peak at calcination temperature of 800 °C and became higher at calcination temperature of 900 °C. However, the diffraction peaks of IWI catalysts calcined at 1,000 °C became lower.

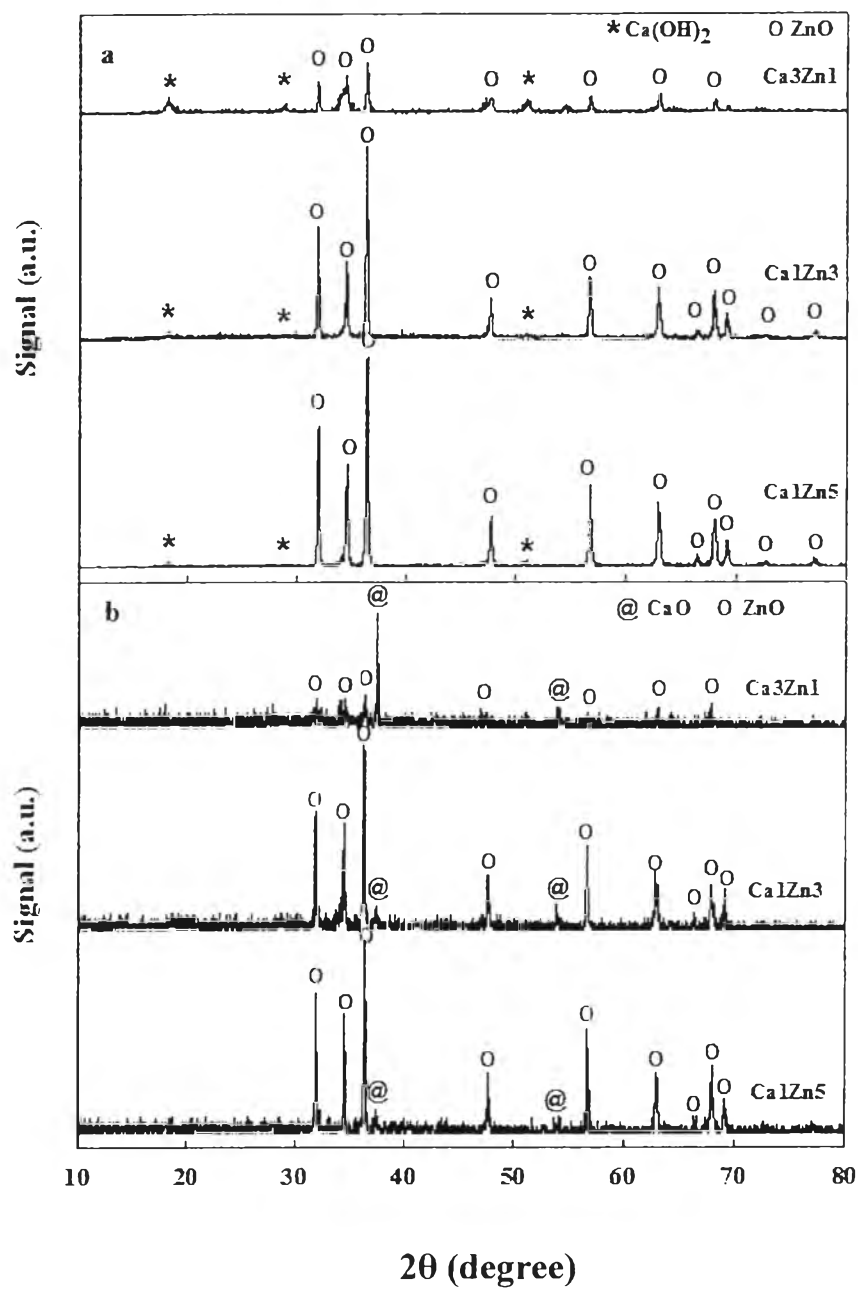


Figure 4.1 XRD patterns of ZnO and Ca-Zn mixed oxides catalysts with various Ca:Zn atomic ratios: a) CP calcined at 800 °C and b) IWI calcined at 900 °C catalysts.

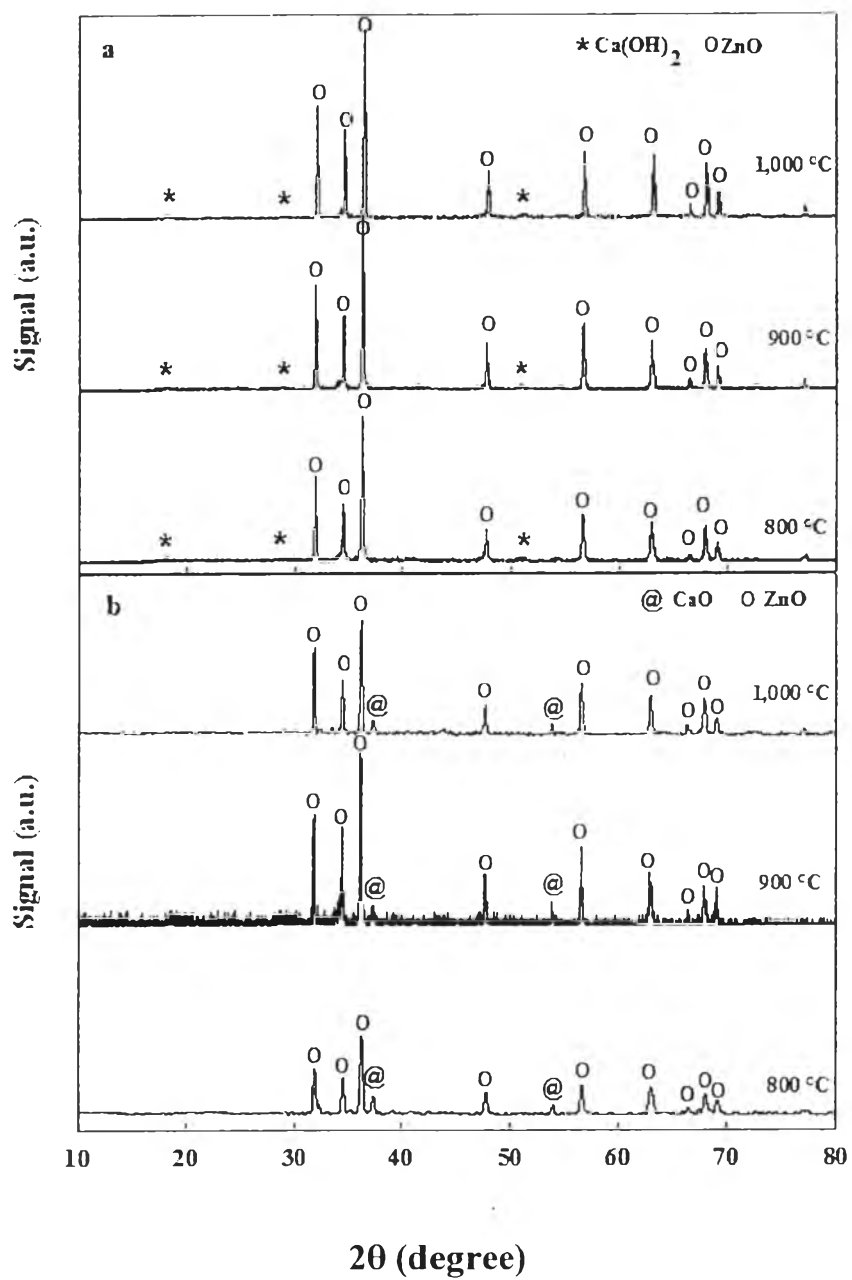


Figure 4.2 XRD patterns of Ca_1Zn_3 catalysts calcined at different temperatures: a) CP and b) IWI techniques.

Table 4.1 Chemical-physical properties of the CaO–ZnO catalysts

Samples	Calcination temperature (°C)	Crystallite size (nm) ^a			CaO–ZnO particle sizes (μm) ^b
		CaO*	Ca(OH) ₂ **	ZnO***	
<i>Co-precipitation</i>					
CaO-ZnO (1:5)	800 (6 h)	-	12.52	32.80	0.21
CaO-ZnO (1:3)	800 (6 h)	-	15.17	32.93	0.25
CaO-ZnO (1:1)	800 (6 h)	-	18.67	34.87	0.29
CaO-ZnO (3:1)	800 (6 h)	-	34.42	35.78	0.35
CaO-ZnO (1:3)	900 (6 h)	-	28.34	29.29	0.40
CaO-ZnO (1:3)	1,000 (6 h)	-	42.38	39.97	0.79
<i>Incipient wetness impregnation</i>					
CaO-ZnO (1:5)	900 (6 h)	36.04	-	35.75	0.40
CaO-ZnO (1:3)	900 (6 h)	36.85	-	37.63	0.52
CaO-ZnO (1:1)	900 (6 h)	38.55	-	37.97	0.52
CaO-ZnO (3:1)	900 (6 h)	49.24	-	51.03	0.54
CaO-ZnO (1:3)	800 (6 h)	29.93	-	27.53	0.26
CaO-ZnO (1:3)	1,000 (6 h)	44.71	-	39.72	0.64

^aCalculated from the Scherrer's equation.^bEstimated from SEM images.

* Averaged from the diffractions of 32.37°, 37.62°, and 53.99°.

** Averaged from the diffractions of 18.17°, and 28.67°

*** Averaged from the diffractions of 31.76°, 34.42°, and 36.25°.

4.1.2 BET Method

The textural properties of the CaO-ZnO catalysts with various Ca:Zn atomic ratio and calcination temperature were characterized by Brunauer–Emmett–Teller (BET) method and the results are given in Table 4.2. For CP catalysts, an increase in Ca loading can cause the decreasing of the specific surface area, pore size, and pore volume. The highest specific surface area of the CaO-ZnO prepared by CP method was 10.65 m²/g at a 1:5 Ca:Zn atomic ratio and decreased to 8.09, 7.33, and 6.16 m²/g for a catalyst with Ca:Zn atomic ratio of 1:3, 1:1, and 3:1, respectively. This kind of phenomenon has already been reported elsewhere (Ngamcharussrivichai *et al*, 2008). At low Ca loading, the small round-shape particles with similar diameter to pure ZnO were observed, while at high Ca loading exhibited large particles with the shape and size close to those of pure CaO. It is likely that at higher amount of Ca may result in agglomeration of active phase occurred during calcination and hence lowering the surface areas of active components. An increase of calcination temperature of catalyst brings to a decrease in the specific surface area from 7.33 m²/g at calcination temperature of 800 °C to 5.63 and 3.10 m²/g at calcination temperature of 900 and 1,000 °C, respectively. The shape of the isotherm and the presence of a hysteresis loop at high relative pressure for CP catalyst at 1:3 Ca:Zn atomic ratio (Figure 4.3a) suggest that the CaO-ZnO framework prepared by CP method can be ascribed to type IV of the IUPAC classification (Sing, 1982). It is essentially mesoporous with some macropores. Moreover, the hysteresis loop has characteristics of H1 types, indicating that the CaO-ZnO framework prepared by CP method consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distributions of pore with 18.22 nm of a pore size.

For IWI catalyst, when a Ca:Zn atomic ratio of catalyst was increased from 1:5 to 1:3, the specific surface area increased from 1.12 to 2.60 m²/g. However, when Ca:Zn atomic ratio of catalyst increase over 1:3, the specific surface area decreased. This was consistent with the appearance of CaO agglomeration, as same as the CP catalysts. For the hysteresis loop of the IWI catalyst at 1:3 Ca:Zn atomic ratio is shown in Figure 4.3b. It is essentially mesoporous with some macropores like CP catalysts. The hysteresis loop has characteristics of H1 types, indicating that the

CaO-ZnO prepared by IWI method framework is the same with the CaO-ZnO framework prepared by CP method. A pore size of CaO-ZnO prepared by IWI method is 17.69 nm.

Table 4.2 Textural properties of the CaO-ZnO catalysts

Sample	Calcination Temperature (°C)	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)
<i>Co-precipitation</i>				
CaO-ZnO (1:5)	800	10.65	0.0640	24.03
CaO-ZnO (1:3)	800	8.09	0.0421	20.82
CaO-ZnO (1:1)	800	7.33	0.0334	18.22
CaO-ZnO (3:1)	800	6.16	0.0266	17.32
CaO-ZnO (1:3)	900	5.63	0.0244	17.34
CaO-ZnO (1:3)	1,000	3.10	0.0112	14.52
<i>Incipient wetness impregnation</i>				
CaO-ZnO (1:5)	900	1.12	0.0042	15.20
CaO-ZnO (1:3)	900	2.60	0.0115	17.69
CaO-ZnO (1:1)	900	1.36	0.0038	11.20
CaO-ZnO (3:1)	900	0.91	0.0031	13.54
CaO-ZnO (1:3)	800	2.68	0.0084	12.53
CaO-ZnO (1:3)	1,000	1.08	0.0045	16.70

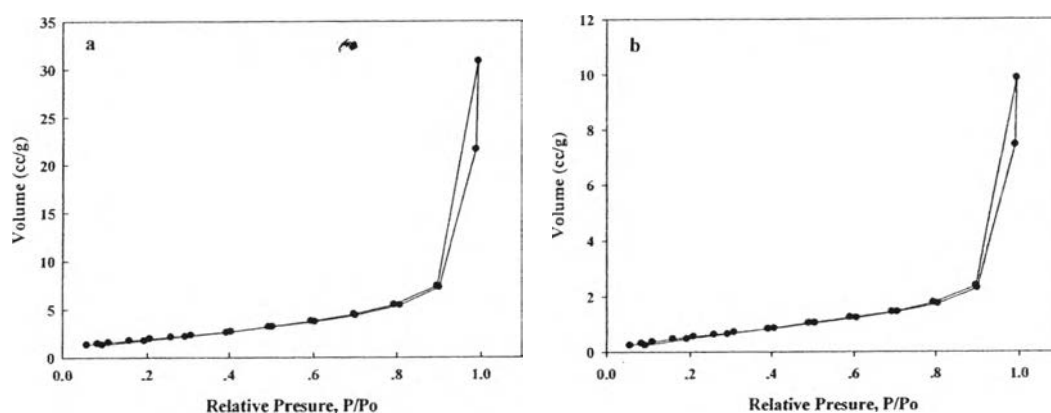


Figure 4.3 N₂ adsorption–desorption isotherms of the CaO-ZnO catalyst prepared by a) CP and b) IWI method.

Effect of precursor concentration and type of precipitant to the textural properties of catalyst are shown in Table 4.3. For ZnO support, it was found that particle size decreased while surface area increased with an increase in Zn precursor concentration. Wang *et al* (2010) found that when the concentration was high, it resulted in a high supersaturation ratio. Crystal nucleation was thus far superior to growth, leading to the formation of crystals of small size and also enhanced BET surface area. When the Ca metal was loaded into ZnO support, surface area decreased because ZnO support particles were covered by CaO. However, surface area of the IWI catalysts exhibited the same trend with ZnO support prepared with various Zn precursor concentrations.

For CP catalysts, when the Ca and Zn precursor concentration was increased in catalyst preparation by co-precipitation, particle size of the CP catalysts decreased while surface area increased, as same as ZnO support. At high Ca and Zn precursor concentrations, the supersaturation solution occurred. When the precipitant was added, crystal nucleation step occurred easily than growth of particle step. So, particle size of the CP catalysts is small.

Table 4.3 Textural properties of the CaO-ZnO catalysts

Sample	Preparation Condition	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)	Particle Size ^a (μm)
<i>ZnO support</i>					
ZnO (900 °C)	0.5M Zn precursor + 0.5M Na ₂ CO ₃	2.47	0.0061	9.88	0.27
ZnO (900 °C)	1M Zn precursor + 0.5M Na ₂ CO ₃	3.26	0.0094	11.53	0.23
ZnO (900 °C)	2M Zn precursor + 0.5M Na ₂ CO ₃	3.32	0.0095	11.67	0.21
ZnO (900 °C)	0.5M Zn precursor + 0.5M NaOH	2.64	0.0066	9.83	0.20
ZnO (900 °C)	1M Zn precursor + 0.5M NaOH	3.35	0.0097	11.09	0.16
ZnO (900 °C)	2M Zn precursor + 0.5M NaOH	3.58	0.0096	11.82	0.14
<i>Incipient wetness impregnation</i>					
CaO-ZnO (1:3, 900 °C)	0.5M Zn precursor + 0.5M Na ₂ CO ₃	1.41	0.0062	17.64	0.48
CaO-ZnO (1:3, 900 °C)	1M Zn precursor + 0.5M Na ₂ CO ₃	1.74	0.0058	13.22	0.42
CaO-ZnO (1:3, 900 °C)	2M Zn precursor + 0.5M Na ₂ CO ₃	1.81	0.0066	12.98	0.38
CaO-ZnO (1:3, 900 °C)	0.5M Zn precursor + 0.5M NaOH	1.99	0.0111	22.39	0.42
CaO-ZnO (1:3, 900 °C)	1M Zn precursor + 0.5M NaOH	2.60	0.0115	17.69	0.42
CaO-ZnO (1:3, 900 °C)	2M Zn precursor + 0.5M NaOH	2.63	0.0115	17.43	0.40
<i>Co-precipitation</i>					
CaO-ZnO (1:3, 800 °C)	0.5M precursor + 0.5M Na ₂ CO ₃	6.58	0.0370	22.45	0.25
CaO-ZnO (1:3, 800 °C)	1M precursor + 0.5M Na ₂ CO ₃	6.64	0.0325	19.56	0.21
CaO-ZnO (1:3, 800 °C)	2M precursor + 0.5M Na ₂ CO ₃	7.33	0.0334	18.22	0.18
CaO-ZnO (1:3, 800 °C)	0.5M precursor + 0.5M NaOH	N.A.	N.A.	N.A.	0.21
CaO-ZnO (1:3, 800 °C)	1M precursor + 0.5M NaOH	N.A.	N.A.	N.A.	0.13
CaO-ZnO (1:3, 800 °C)	2M precursor + 0.5M NaOH	N.A.	N.A.	N.A.	0.12

^aEstimated from SEM images.

4.1.3 X-ray Fluorescence Spectroscopy (XRF)

The chemical compositions of the samples were summarized in Table 4.4. The synthesized catalysts have the values of metal concentrations closely to those of expected values.

Table 4.4 Chemical compositions of fresh catalysts by using XRF measurement.

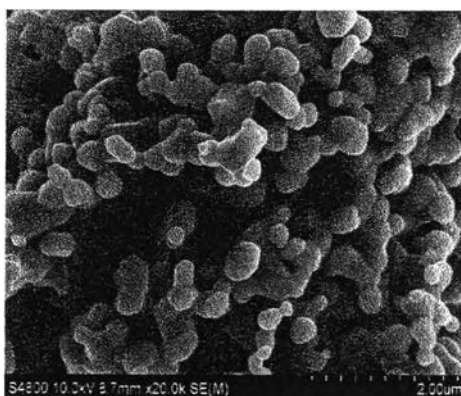
Samples	Calcination temperature (°C)	Element compositions (wt%)		Synthesized Ca/Zn ^a	Expected Ca/Zn
		Ca	Zn		
<i>Co-precipitation</i>					
CaO–ZnO (1:5)	800 (6 h)	10.40	89.60	0.12	0.20
CaO–ZnO (1:3)	800 (6 h)	16.64	83.36	0.20	0.33
CaO–ZnO (3:1)	800 (6 h)	86.76	13.24	3.56	3.00
CaO–ZnO (1:3)	900 (6 h)	14.19	85.81	0.17	0.33
CaO–ZnO (1:3)	1,000 (6 h)	14.57	85.43	0.17	0.33
<i>Incipient wetness impregnation</i>					
CaO–ZnO (1:5)	900 (6 h)	12.47	87.53	0.14	0.20
CaO–ZnO (1:3)	900 (6 h)	27.85	72.15	0.39	0.33
CaO–ZnO (3:1)	900 (6 h)	57.62	42.38	3.36	3.00
CaO–ZnO (1:3)	800 (6 h)	12.87	87.13	0.15	0.33
CaO–ZnO (1:3)	1,000 (6 h)	16.56	83.44	0.20	0.33

^ameasured by XRF measurement.

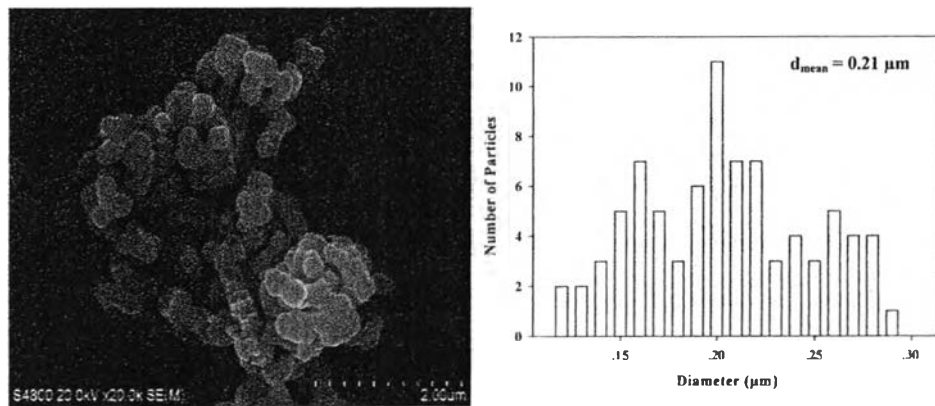
4.1.4 Scanning Electron Microscope (SEM)

According to the morphology and particle size of the catalysts, as imaged in Figures 4.4 and 4.5, the CaO-ZnO particles have particle size of about 0.2–0.8 μm for CP catalysts and 0.4–0.6 μm for IWI catalysts with spherical shape. It was found that the particle size of the CaO-ZnO catalysts increased with increasing the Ca loading for both CP and IWI catalysts. At low Ca loading, the very fine CaO-ZnO particles were observed. However, the agglomeration of particles occurred when the Ca:Zn atomic ratio was increased to 3:1.

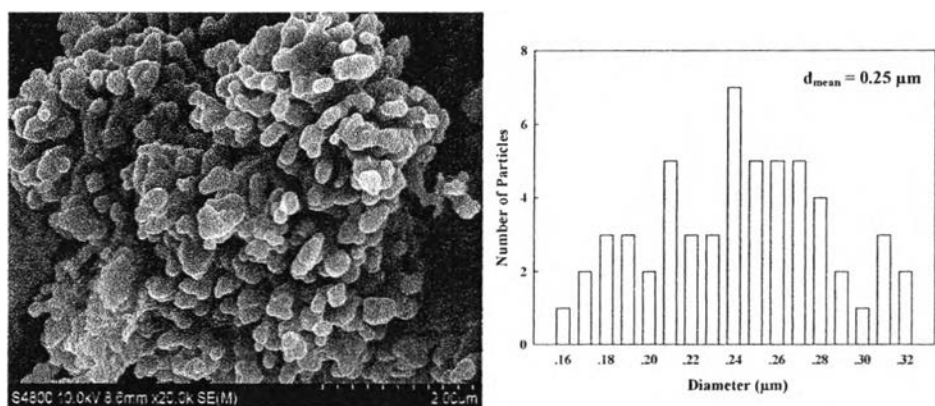
In the part of discussion, the catalytic activity of CP catalysts increased when the particle size increased from 0.21 μm (Ca:Zn = 1:5) to 0.25 μm (Ca:Zn = 1:3). However, the catalytic activity of CP catalysts are constant at the particle size is over 0.25 μm . As same as the CP catalysts, the catalytic activity of IWI catalysts increased when the particle size increased from 0.40 μm (Ca:Zn = 1:5) to 0.52 μm (Ca:Zn = 1:3) and stable when the particle size is over 0.52 μm .



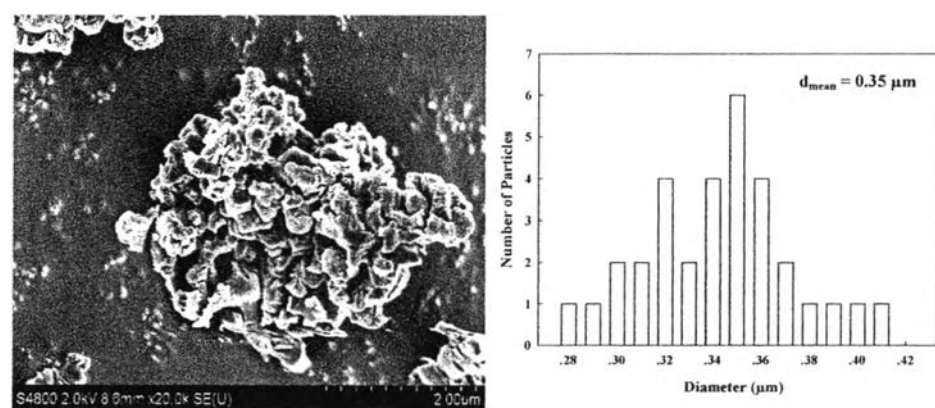
ZnO catalyst



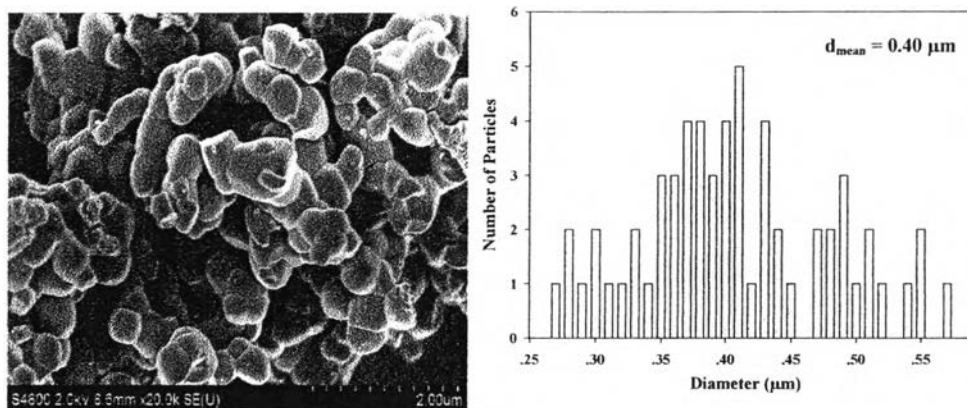
CaO-ZnO (1:5, CP) catalyst



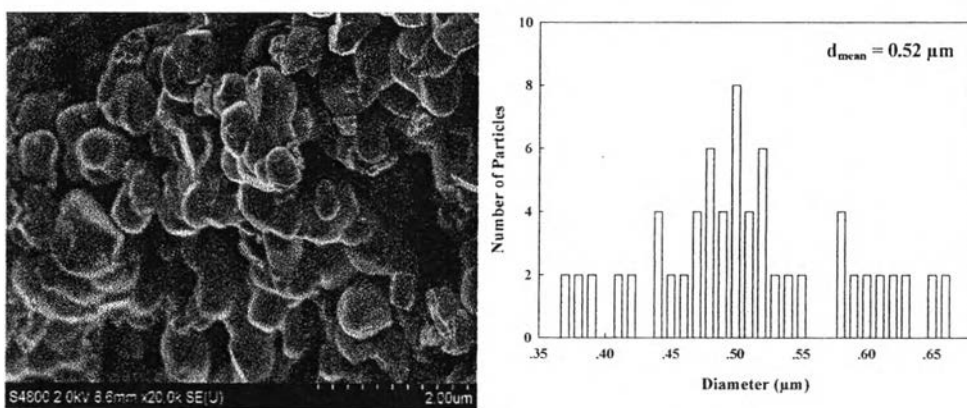
CaO-ZnO (1:3, CP) catalyst



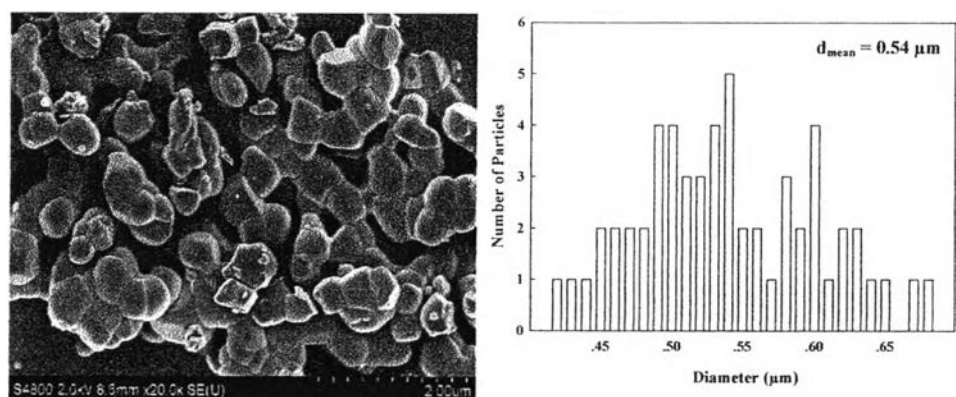
CaO-ZnO (3:1, CP) catalyst



CaO-ZnO (1:5, IWI) catalyst



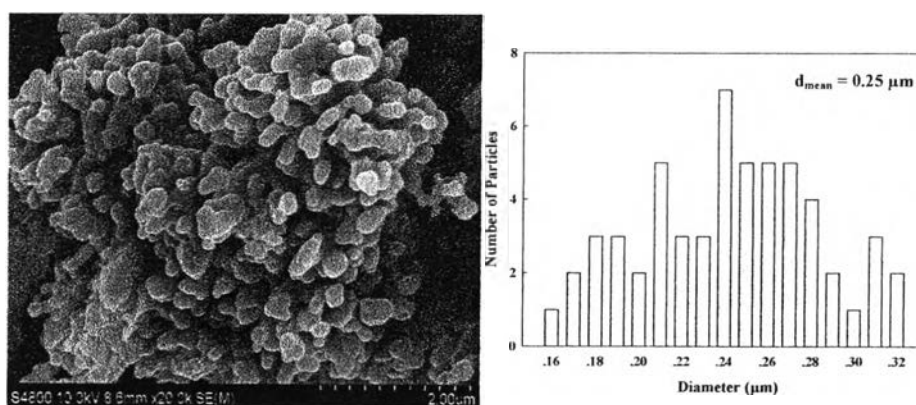
CaO-ZnO (1:3, IWI) catalyst



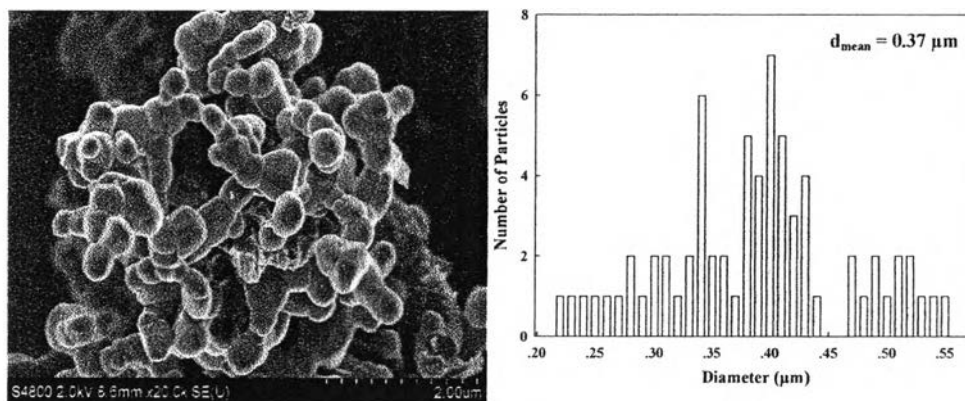
CaO-ZnO (3:1, IWI) catalyst

Figure 4.4 SEM images of ZnO and Ca-Zn mixed oxides catalysts with various Ca:Zn atomic ratios.

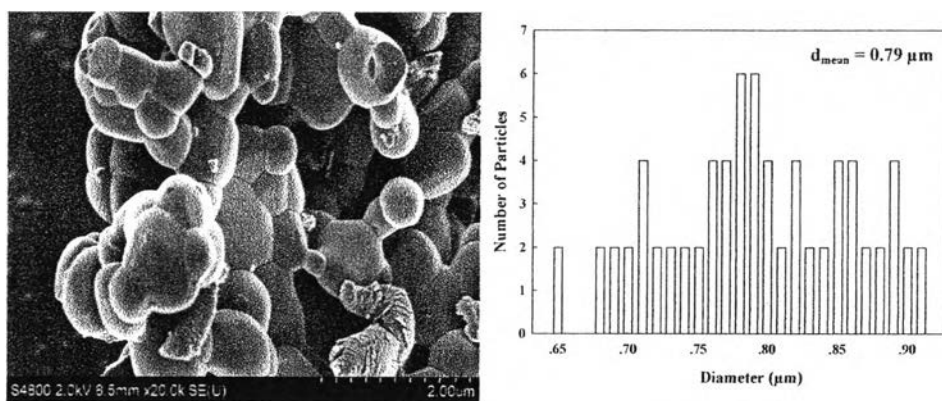
When varying calcination temperature of the CaO–ZnO (Ca:Zn = 1:3) catalysts, the SEM images (Figure 4.5) revealed that the particle size of CaO–ZnO catalysts increased with increasing calcination temperature. However, the positive result of increasing calcination temperature was to provide the optimum size of CaO particle in the catalyst, which might be suitable for the reaction. In terms of electronic effect, Ngamcharussrivichai and coworker (2008) also proposed that the calcination temperature of 600 °C, which is required for the decomposition of CaCO₃ to form CaO, the lower the energy that is consumed in the preparation of active catalyst. For the negative structural change, the highest calcination temperature of 900°C definitely represented the agglomeration of CaO cluster, which could block the active site of the catalyst, so the catalyst was finally deactivated. It can be concluded that the suitable thermal treatment for preparing the active CaO–ZnO catalyst belonged to 800 °C for the catalysts prepared by CP method and 900 °C for the catalysts prepared by IWI method.



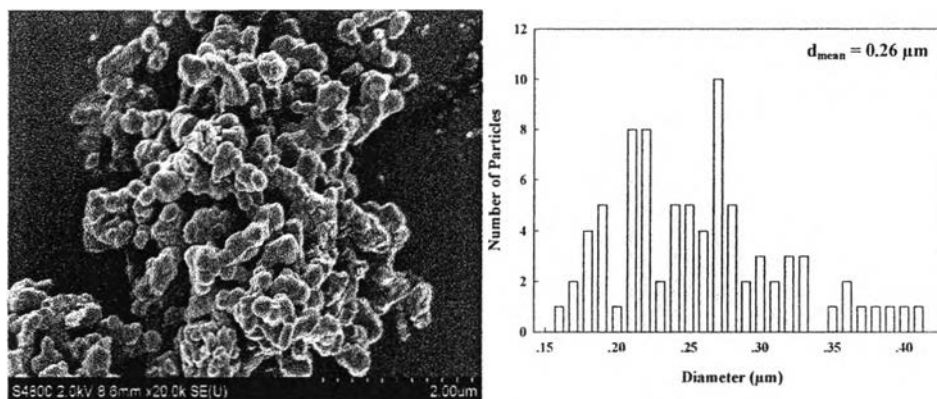
CaO–ZnO (1:3, CP, calcined at 800 °C) catalyst



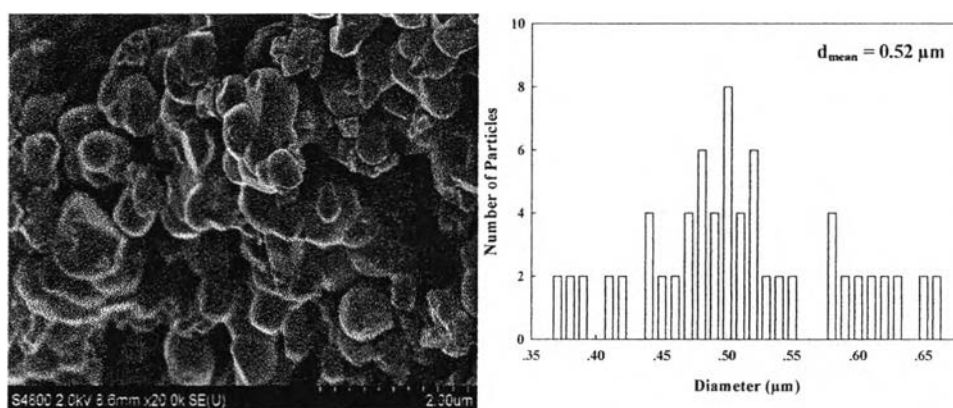
CaO-ZnO (1:3, CP, calcined at 900 °C) catalyst



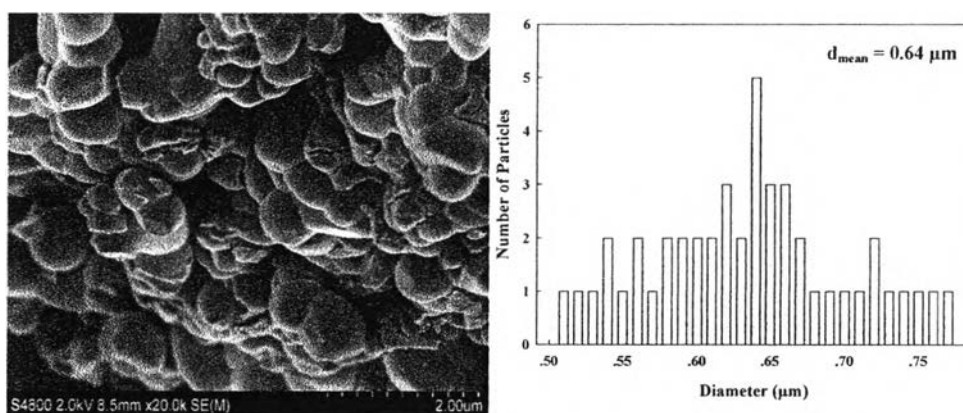
CaO-ZnO (1:3, CP, calcined at 1,000 °C) catalyst



CaO-ZnO (1:3, IWI, calcined at 800 °C) catalyst



CaO-ZnO (1:3, IWI, calcined at 900 °C) catalyst



CaO-ZnO (1:3, IWI, calcined at 1,000 °C) catalyst

Figure 4.5 SEM images of CaO-ZnO (Ca:Zn = 1:3) catalysts with various calcination temperatures.

4.1.5 Temperature-Programmed Reduction (TPR)

The TPR profiles of CaO–ZnO catalysts with various Ca:Zn atomic ratios were shown in Figure 4.6 (CP) and Figure 4.7 (IWI). ZnO support did not present reduction peaks, which was probably the result of complete dehydroxylation and high thermal stability (Valenzuela *et al*, 2002). While, CaO exhibited the reduction peak at temperature about 630 °C (Bellido *et al*, 2009). When adding Ca to form the Ca–Zn binary system of CP catalysts, the reduction peaks were observed (Figure 4.8). At 1:5 Ca:Zn atomic ratio, the reduction peak of CP catalyst was slightly shifted from 630 to 670 °C which similar to the reduction peak of pure CaO. This means that Ca and Zn have low interaction. When the Ca amount of CP catalyst was increased from 1:5 to 1:3 Ca:Zn atomic ratio, the reduction peak was shifted to higher temperature (790 °C). It implies that a at Ca:Zn atomic ratio of 1:3, the interaction between Ca and Zn is highest. At a Ca:Zn atomic ratio of 1:1, the reduction peak was shifted to lower temperature (715 °C). The interaction between Ca and Zn become lower after increasing Ca:Zn atomic ratio to 1:1. Finally, after increasing Ca:Zn atomic ratio to highest amount (3:1), the reduction peak was shifted to lower temperature (665 °C) which similar to the reduction peak of Ca(OH)₂. It shows that the interaction between Ca and Zn become lower. Thus, the CP catalyst at 1:3 Ca:Zn atomic ratio exhibits good interaction between Ca and Zn.

In the case of IWI catalysts, no significant differences among the reduction peaks of each Ca:Zn atomic ratio were observed, even the area of the reduction peaks. In some cases, it has been proposed that the area of the reduction peak could relate the dispersion of metal briefly (Biswas and Kunzru, 2007). From Figure 4.7, the IWI catalyst at a Ca:Zn atomic ratio of 1:3 shows high reduction peak area than the others. While, the dispersion of CaO particles of the IWI catalysts at high Ca:Zn atomic ratio (1:1 and 3:1) became lower because of its low reduction peak area. This could be related with the agglomeration of CaO particle during the Ca variation. So, the IWI catalyst at 1:3 Ca:Zn atomic ratio exhibits good properties than the others.

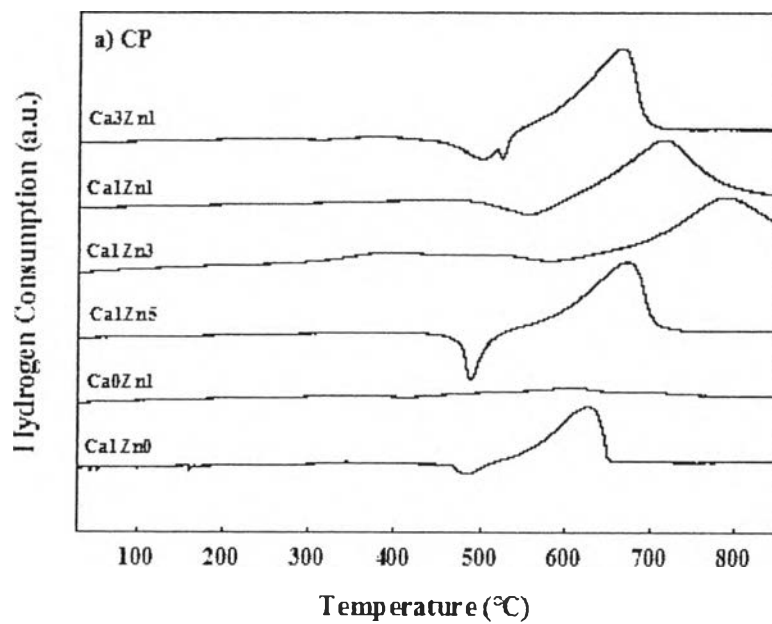


Figure 4.6 TPR profiles of ZnO and Ca–Zn mixed oxides with various Ca:Zn atomic ratios of the catalysts prepared by CP method.

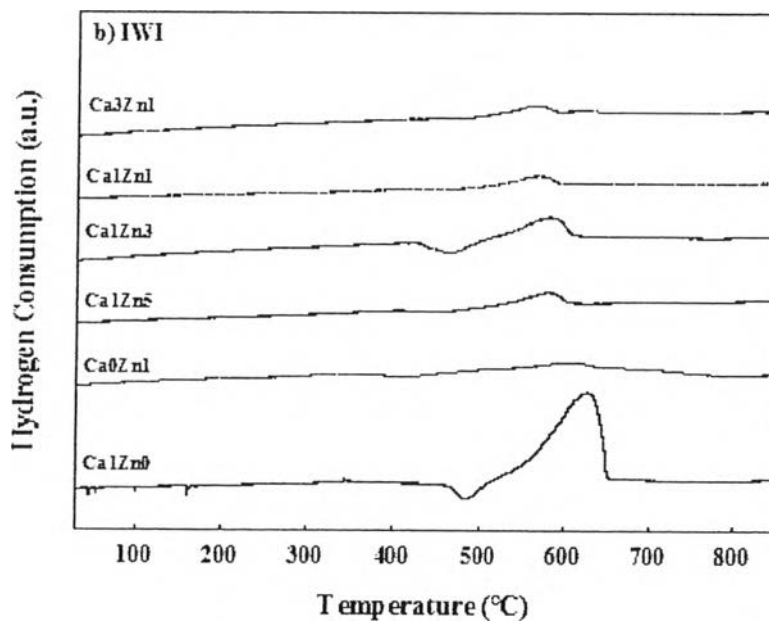


Figure 4.7 TPR profiles of Ca–Zn mixed oxides with various Ca:Zn atomic ratios of the catalysts prepared by IWI method.

From Figures 4.8 and 4.9, the effect of calcination temperature on the catalytic activity was also studied for the catalysts prepared by CP and IWI method, respectively. The CP catalysts calcined at 800 °C, the reduction peak shifted toward higher temperature compared with reduction peak of pure CaO and ZnO. This phenomenon exhibited the high interaction between metal and support after mixing together. At high thermal treatment (900 °C), the reduction peak was shifted to lower temperature which similar to the reduction peak of pure Ca(OH)₂. It shows lower interaction between metal and support and seems to separate from each other. At the highest thermal temperature treatment (1,000 °C), the reduction peak was similar to the reduction peak of pure CaO and ZnO. Moreover, the area of hydrogen consumed was the lowest since the CaO would undergo sintering at this condition (Biswas and Kunzru, 2007).

In the case of the IWI catalysts (Figure 4.9), the reduction peaks of each calcination temperature have no significant differences. However, the areas of hydrogen consumed are different. The IWI catalysts calcined at 800 and 900 °C show reduction peak at 600 °C with high peak area compared with the IWI catalyst calcined at 1,000 °C. It shows that the dispersion of CaO particles became lower when calcined at 1,000 °C because of its low reduction peak area. This could be related with the agglomeration of CaO particle in the high thermal treatment temperature.

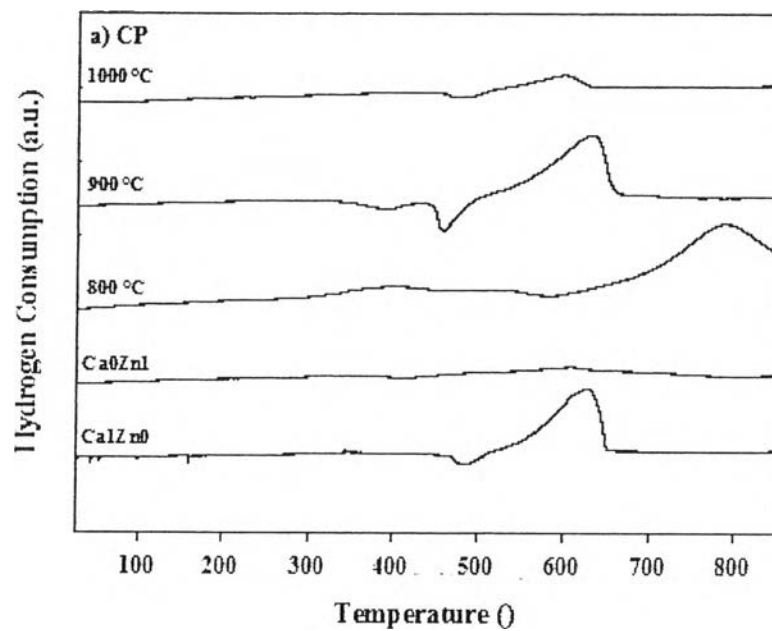


Figure 4.8 TPR profiles of Ca_1Zn_3 catalysts prepared by CP method with different calcination temperatures.

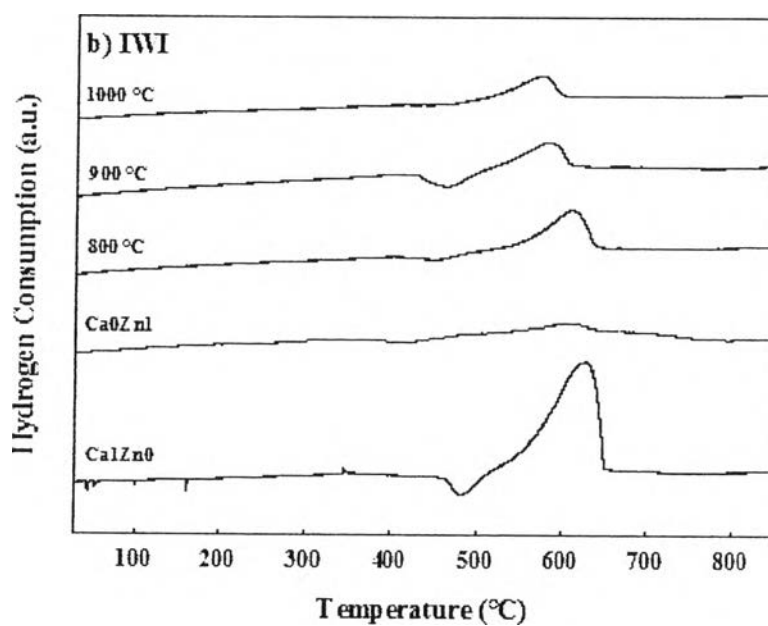


Figure 4.9 TPR profiles of Ca_1Zn_3 catalysts prepared by IWI method with different calcination temperatures.

4.1.6 Hammett Indicator

The basic strength (H_{-}) and total basicity of the CaO-ZnO catalysts was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 mol/l anhydrous methanol solution) titration: bromothymol Blue ($H_{-}=7.2$), phenolphthalein ($H_{-}=9.8$), Tropaeolin ($H_{-}=11$), 2,4-dinitroaniline ($H_{-}=15$), and 4-nitroaniline ($H_{-}=18.4$) (Gorzawski and Hoelderich, 1999) and shown in Table 4.5. In term of basic strength (H_{-}), all of the catalysts in both preparation techniques achieved high basic strength in the range of 11.0–15.0 with the total basicity of 8.8040 and 6.8619 mmol/g for IWI and CP catalysts, respectively.

Both IWI and CP catalysts, when increasing the Ca:Zn atomic ratio or Ca amount, total basicity of these catalysts increased. For IWI catalyst, CaO-ZnO calcined at 900 °C exhibited the highest total basicity compared with 800 and 1,000 °C. For CP catalysts, CaO-ZnO calcined at 800 °C exhibited the highest total basicity. Especially, the basicity of catalysts prepared by IWI method exhibited higher values than those of CP method in all of Ca:Zn ratios. However, basic strength and basicity of the catalysts are not the only one factor that affects to the reaction yield since the FAME yield of IWI catalysts did not show higher values than those of CP catalysts. The specific BET surface area should be discussed as one of factors that affected to transesterification.

Table 4.5 Summarization of basic strength and basicity of the fresh catalysts.

Sample	Temperature (°C)	Basicity (mmol/g)				Total basicity (mmol/g)
		$7.2 < H_- < 9.8$	$9.8 < H_- < 11$	$11 < H_- < 15$	$15 < H_- < 18.4$	
<i>Incipient wetness impregnation (IWI)</i>						
CaO-ZnO (1:5)	900	0.4962	0.1527	5.2099	-	5.8588
CaO-ZnO (1:3)	900	0.4314	0.6667	7.7059	-	8.8040
CaO-ZnO (1:1)	900	0.2026	2.6151	16.1142	-	18.9319
CaO-ZnO (3:1)	900	0.5100	2.8051	26.2659	-	29.5774
CaO-ZnO (1:3)	800	0.2268	0.4128	6.7297	-	7.3653
CaO-ZnO (1:3)	1,000	0.2174	0.1661	5.2797	-	5.6632
<i>Co-precipitation (CP)</i>						
CaO-ZnO (1:5)	800	0.6744	0.2312	3.3911	-	4.2967
CaO-ZnO (1:3)	800	1.0476	0.2857	5.5286	-	6.8619
CaO-ZnO (1:1)	800	1.1176	0.6078	12.2157	-	13.9411
CaO-ZnO (3:1)	800	1.5926	1.5556	19.7222	-	22.8704
CaO-ZnO (1:3)	900	0.3669	0.2385	4.5298	-	5.1352
CaO-ZnO (1:3)	1,000	0.2385	0.1853	3.4495	-	3.8733

6.1.7 Temperature-Programmed Desorption of CO₂ (TPD-CO₂)

The total basicity and basic site distributions were evaluated by using temperature-programmed desorption of CO₂. The CO₂-TPD profiles of the CaO-ZnO catalysts prepared by both CP and IWI methods were displayed in Figures 4.10 and 4.11. The TPD patterns of the CaO-ZnO catalysts prepared by CP method (Figure 4.10) showed CO₂ desorption peaks at the temperature ranging from 400 to 600 °C and 600 to 850 °C. Serio *et al.* (2006) explained that a very broad desorption band extending from 400 to 600 °C could be assigned as interaction of CO₂ with sites of weak and medium basic strengths. The narrower band at higher temperature between 600 and 850 °C can be attributed to the presence of much stronger basic site. When the Ca amounts or Ca:Zn atomic ratio increased from 1:5 to 3:1, the CO₂ desorption peaks of both weak and strong basic strength become higher intensity. In addition, the weak desorption peak was shifted into lower temperature, while the strong desorption peak was shifted into higher temperature. This situation shows the interaction between Ca and Zn when increase the Ca amounts or Ca:Zn atomic ratio. For the CO₂-TPD profiles of the CaO-ZnO catalysts prepared by IWI method (Figure 4.11), the CO₂ desorption peaks occurred at the temperature ranging from 420 to 600 °C for weak basic strength and 600 to 800 °C for strong basic strength. These IWI catalysts have the same situation with CP catalysts. When increasing Ca amounts or Ca:Zn atomic ratio, the CO₂ desorption peaks of both weak and strong basic strength become higher intensity and the weak desorption peak was shifted into lower temperature, while the strong desorption peak was shifted into higher temperature.

For calcination temperature of CaO-ZnO catalysts prepared by CP method, from CO₂-TPD profiles (Figure 4.12) show that the catalyst calcined at 800 °C has high basicity in both weak and strong basic strength of catalyst. When the calcination temperature was increased from 800 °C to 900 °C, peak area of the strong desorption peak decreases. After increasing the calcination temperature until 1,000 °C, peak area of both weak and strong desorption peak largely decreased. This result related with the transesterification reaction activity of catalysts which the calcination temperature of 800 °C shows the highest biodiesel yield compared with 900 and 1,000 °C.

For IWI catalysts, in Figure 4.13, the calcination temperature of 900 °C gave the highest desorption peak areas for both weak and strong desorption peaks. While, at calcination temperature of 800 °C shows lower desorption peak at weak basic strength position. For the calcination temperature of 1,000 °C, both weak and strong desorption peak were very low intensity when compared with the others.

The TPD-CO₂ result of effect of type of precipitant in catalyst preparation by CP method is shown in Figure 4.14, the result shows that the CP catalyst prepared by using NaOH as a precipitant does not have any desorption peak while the CP catalyst prepared by using Na₂CO₃ as a precipitant shows the desorption peaks at 500 and 800 °C. It can be concluded that the CP catalyst prepared by using NaOH as a precipitant give rather low basic properties which related to its low activity in biodiesel production.

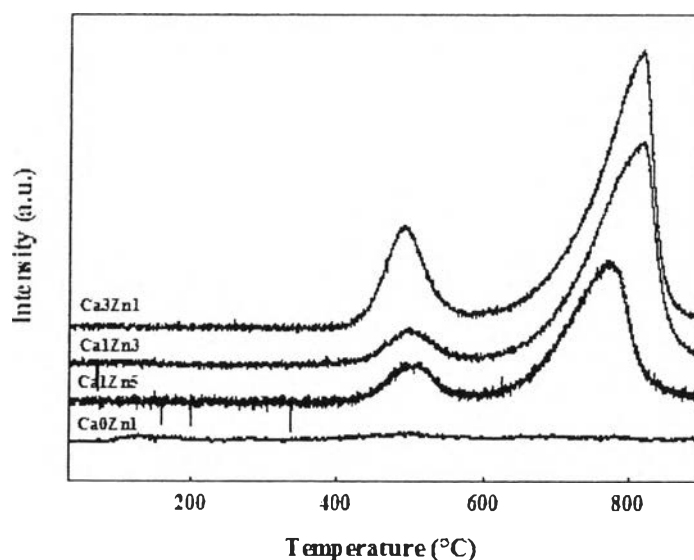


Figure 4.10 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by CP method with various Ca:Zn atomic ratio.

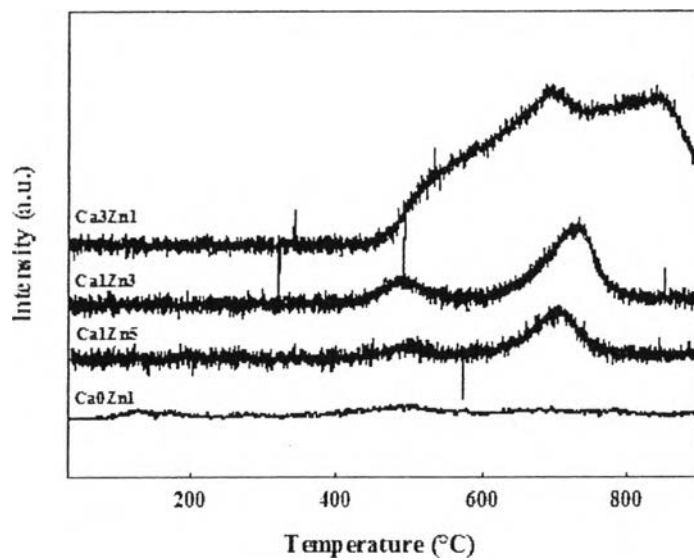


Figure 4.11 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by IWI method with various Ca:Zn atomic ratio.

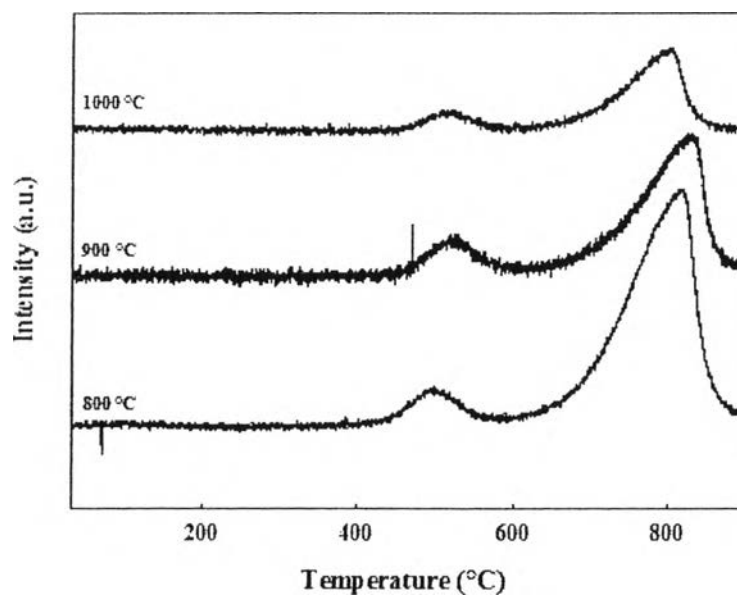


Figure 4.12 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by CP method with varying calcination temperature.

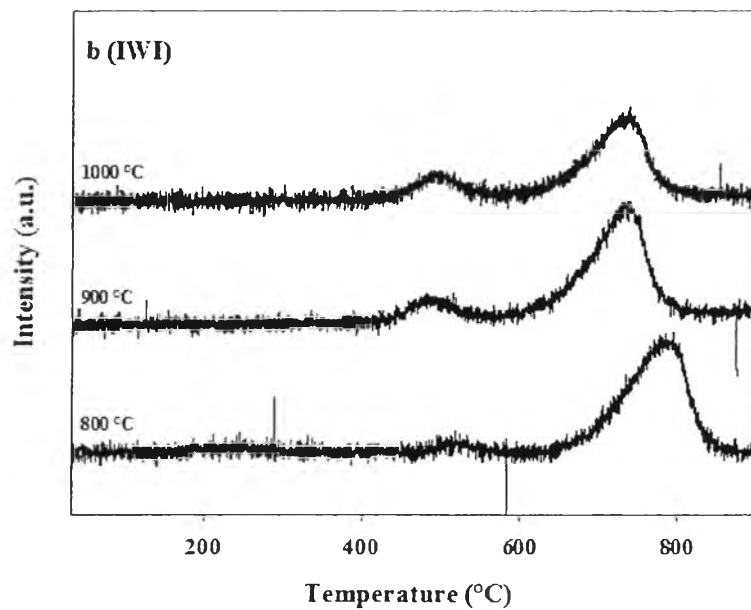


Figure 4.13 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by IWI method with varying calcination temperature.

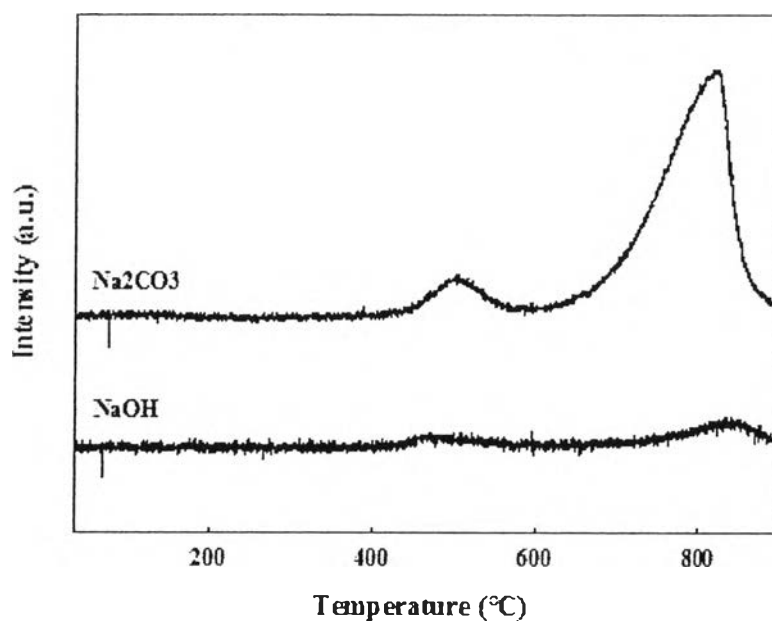


Figure 4.14 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by CP method with varying type of precipitant in preparation step.

4.2 Transesterification Reaction of Fresh Catalyst

CaO–ZnO was used as a heterogeneous basic catalyst in the transesterification reaction. To investigate the optimum conditions of these catalysts in transesterification of palm oil, the starting conditions of transesterification reaction over CaO–ZnO catalyst were 60 °C, 300 rpm of stirrer speed, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt% (based on weight of vegetable oil), and reaction time 8 h.

4.2.1 Effect of Precursor Concentration and Type of Precipitant in Catalyst Preparation

4.2.1.1 *Impregnation Method (IWI)*

For IWI method, ZnO supports were prepared by precipitation method which $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as a precursor, and NaOH and Na_2CO_3 were used as a precipitant. The effect of precursor concentration and type of precipitant in ZnO support preparation for CaO–ZnO catalyst prepared by IWI method on the yield of biodiesel are illustrated in Figure 4.15. The CaO–ZnO (atomic ratio Ca:Zn = 1:3) catalyst was carried out under the conditions of reaction temperature of 60 °C, 300 rpm of stirrer speed, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and reaction time 8 h. From the effect of precursor concentration on ZnO support preparation, Figure 4.15 indicates that the biodiesel yield increased when increasing the concentration of Zn precursor. It can be explained that crystal size decreased with an increase in solution concentration of dispersed feed (Wang *et al.*, 2010). When the precursor concentration was high, it resulted in a high supersaturation ratio of precursor solution. Crystal nucleation was thus far superior to growth, leading to the formation of crystals of small size and also enhanced surface area. For effect of type of precipitant, catalysts prepared by using NaOH as a precipitant in ZnO support preparation gave higher biodiesel yield than the catalysts prepared by using Na_2CO_3 for all of precursor concentrations.

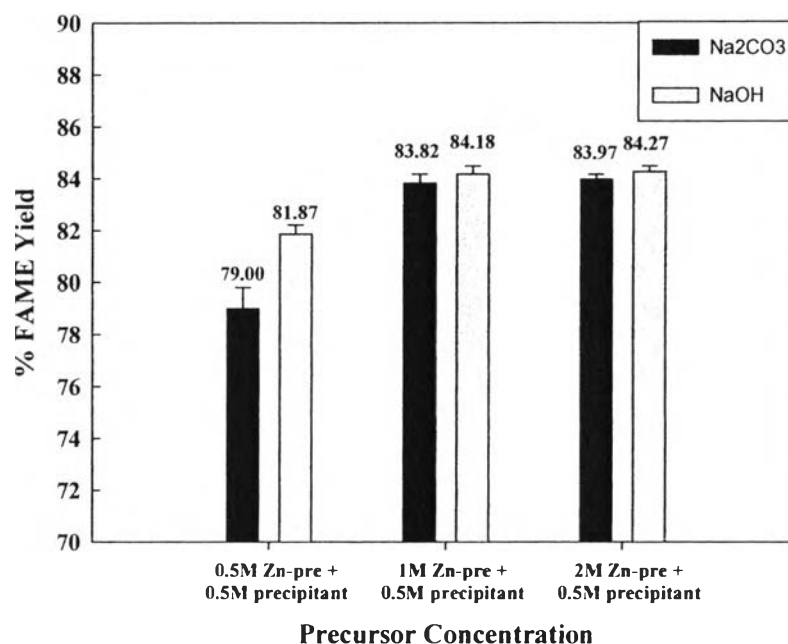


Figure 4.15 Effect of precursor concentration and type of precipitant in ZnO support preparation for CaO-ZnO catalyst prepared by IWI method on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.

4.2.1.2 Co-Precipitation Method (CP)

The effect of precursor concentration in CaO-ZnO catalyst prepared by CP method on the yield of biodiesel is illustrated in Figure 4.16. The reaction was tested by using the same condition as the CaO-ZnO catalyst prepared by IWI method. From the Figure 4.16 indicates that the biodiesel yield increased with increasing the concentration of Ca and Zn precursor. This result was explained by the same evidence with CaO-ZnO catalyst prepared by IWI that crystal size decreased with an increase in solution concentration of precursor.

For the effect of type of precipitant (Figure 4.17), it was found that the CP catalyst prepared by using NaOH as a precipitant exhibited no activity (%FAME yield = 0.85). From TPD-CO₂ result, the CP catalyst prepared by using NaOH showed no desorption peak, suggesting that it has no basic properties.

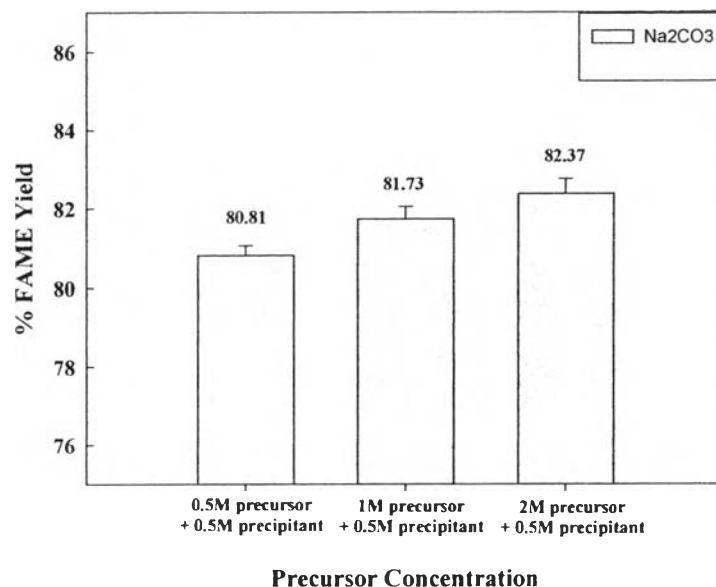


Figure 4.16 Effect of precursor concentration in CaO-ZnO catalyst prepared by CP method on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.

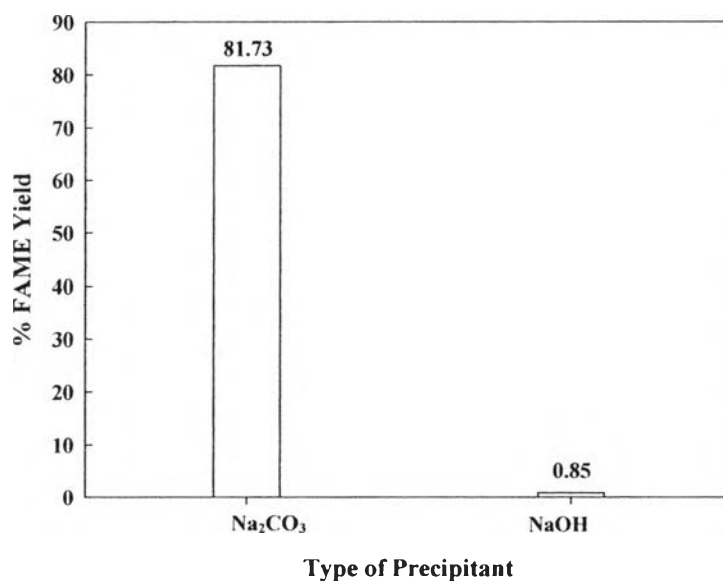


Figure 4.17 Effect of type of precursor in CaO-ZnO catalyst prepared by CP method on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.

4.2.2 Effect of Calcination Temperature

The effect of calcination temperature on the biodiesel yield, as illustrated in Figure 4.18, was tested over the CaO–ZnO (atomic ratio Ca:Zn = 1:3) catalyst under the conditions of reaction temperature of 60 °C, 300 rpm of stirrer speed, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and reaction time 8 h. From the calcination temperature range (800–1,000 °C), Figure 4.18 indicates that catalyst prepared by CP method gave the highest % FAME yield (81.73%) at calcination temperature of 800 °C and % FAME yield decreased after increasing calcination temperature above 800 °C. From Hemmett indicator and TPD-CO₂ results can be explained that the CaO-ZnO calcined at 800 °C gave highest basicity compared with CaO-ZnO calcined at 900 and 1,000 °C. Moreover, BET surface area of CaO-ZnO calcined at 800 °C is the highest compared with 900 and 1,000 °C and decreased respectively when calcination temperature was increased to 900 and 1,000 °C. For the catalysts prepared by IWI method, the calcination temperature of 800 °C showed lower catalytic activities compared to CP catalyst. At the calcination temperature of 900 °C, the catalyst prepared by IWI method gave the highest biodiesel yield over 80 % FAME. However, at the calcination temperature of 1,000 °C shows almost no catalytic activities for both CP and IWI catalysts. From BET surface area of IWI catalysts shows that increasing calcination temperature will decrease surface area of CaO-ZnO which at calcination temperature of 800 °C gave the highest BET surface area of CaO-ZnO and slightly decrease when calcination temperature up to 900 °C. Ngamcharussrivichai and coworker (2008) proposed that increasing calcination temperature up to high temperature could significantly decrease the FAME content since the sintering of CaO particles could be possibly affected. However, basic strength and basicity should be one of important factors that affected to biodiesel yield. From Hemmett indicator and TPD-CO₂ results, the CaO-ZnO calcined at 900 °C gave the highest basicity and basicity decreased at calcination temperature of 800 °C. At calcination temperature of 1,000 °C, the basicity of catalyst rather low, this is probably why at calcination temperature of 1,000 °C gave no biodiesel yield.

According to the results, it should be noted that the catalytic activities of the CaO–ZnO catalysts could be related with the type of catalyst preparation techniques. In summary, the suitable calcination temperature of CaO–ZnO catalysts prepared by CP method was 800 °C, while the catalyst prepared by IWI method exhibited high activity at calcination temperature of 900 °C.

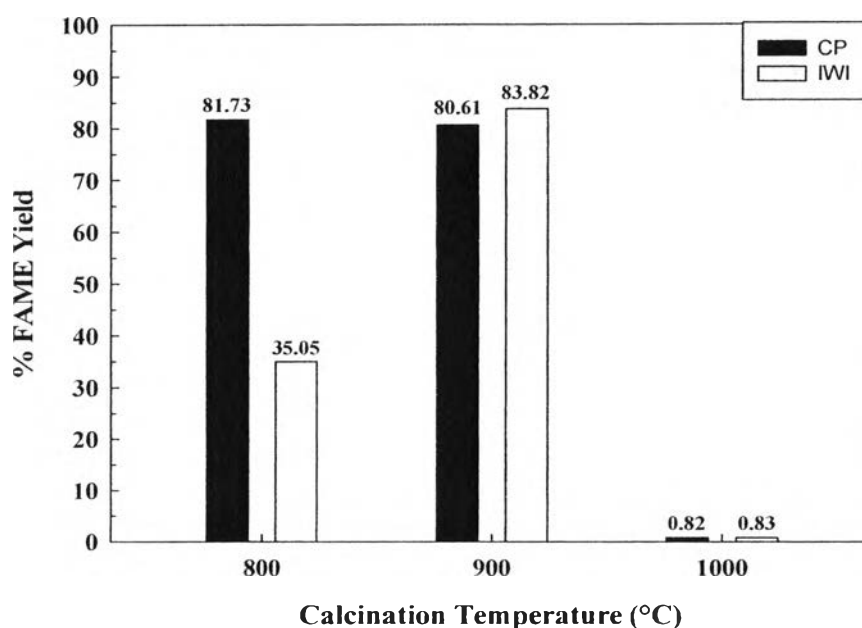


Figure 4.18 Effect of calcination temperature on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.

4.2.3 Effect of Ca:Zn Atomic Ratio

In order to study the effect of catalyst composition on biodiesel yield, the various Ca:Zn atomic ratios were prepared at 1:5, 1:3, 1:1, and 3:1, respectively. From Figure 4.19, the results revealed that the biodiesel yield was greatly effective on the variation of Ca:Zn atomic ratio. For the whole catalysts, the catalytic activity became increasing when higher amounts of CaO (more Ca:Zn) were presented and became steadily when Ca:Zn atomic ratio of catalyst was increased over than 0.33 for both preparation methods. The biodiesel yield of catalysts prepared by IWI method is rather low at the 0.2 Ca:Zn atomic ratio of the CaO–ZnO catalyst.

However, the highest biodiesel, approximately 83%, was found after adding the moderate amount of CaO (Ca:Zn = 0.33), while the average high value of biodiesel yield at 80% were observed on the Ca:Zn of 0.33–3 prepared by CP method. Regarding to the activity of catalyst prepared by IWI technique, the biodiesel yield was decreased slightly in the presence of the high CaO concentrations (Ca:Zn atomic ratio ≥ 0.33). This was consistent with the appearance of CaO agglomeration which has been reported elsewhere (Rubio *et al.*, 2010). The study reveals that an increment of CaO for high wt% does not lead to a better catalytic performance. From Hemmett indicator and TPD-CO₂ results show that increasing of Ca:Zn atomic ratio could increase the basicity of CaO-ZnO. However, BET surface area decreases when increasing Ca:Zn atomic ratio. At 1:3 Ca:Zn atomic ratio should be optimum ratio because both basicity and surface area are obtained in the suitable value.

According to the results, it should be noted that the catalytic activities of the CaO–ZnO catalysts could be related with the Ca:Zn atomic ratio. For instance, the Ca:Zn atomic ratio of the CaO–ZnO catalysts in both methods should be 0.33.

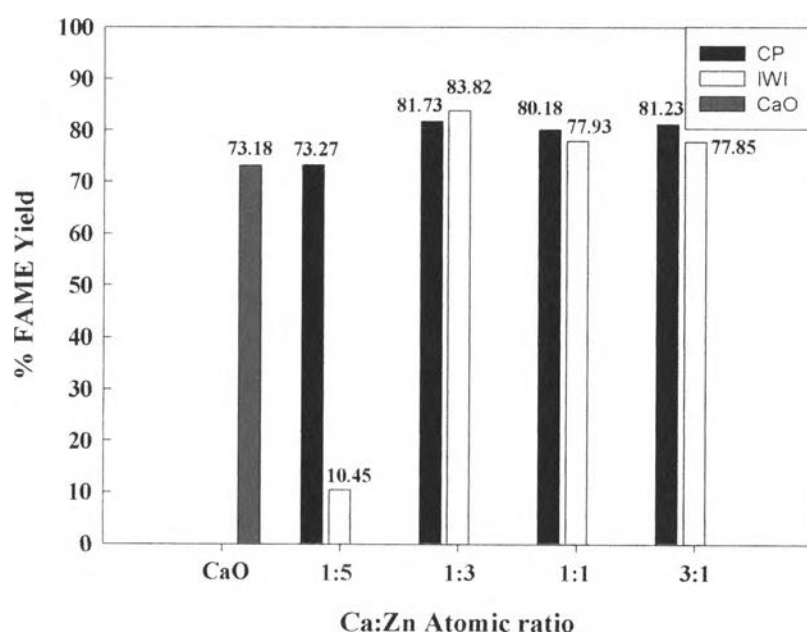


Figure 4.19 Effect of Ca:Zn atomic ratio on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.

4.3 Characterization of Spent Catalyst

4.3.1 X-ray Diffraction (XRD)

Figure 4.20 illustrates The XRD patterns of both fresh and spent catalysts for comparison purposes. The catalysts were continually tested for 3 cycles. For the CP catalysts (Figure 4.20a), it was found that the spent catalysts showed a decrease in $\text{Ca}(\text{OH})_2$ diffraction peak with increase the number of testing cycle. The intensity of CaO for the IWI catalysts (Figure 4.20b) decreased significantly after used in the consecutive runs. It can be suggested that CaO-ZnO catalysts for both CP and IWI methods lose their active site when the run number increases.

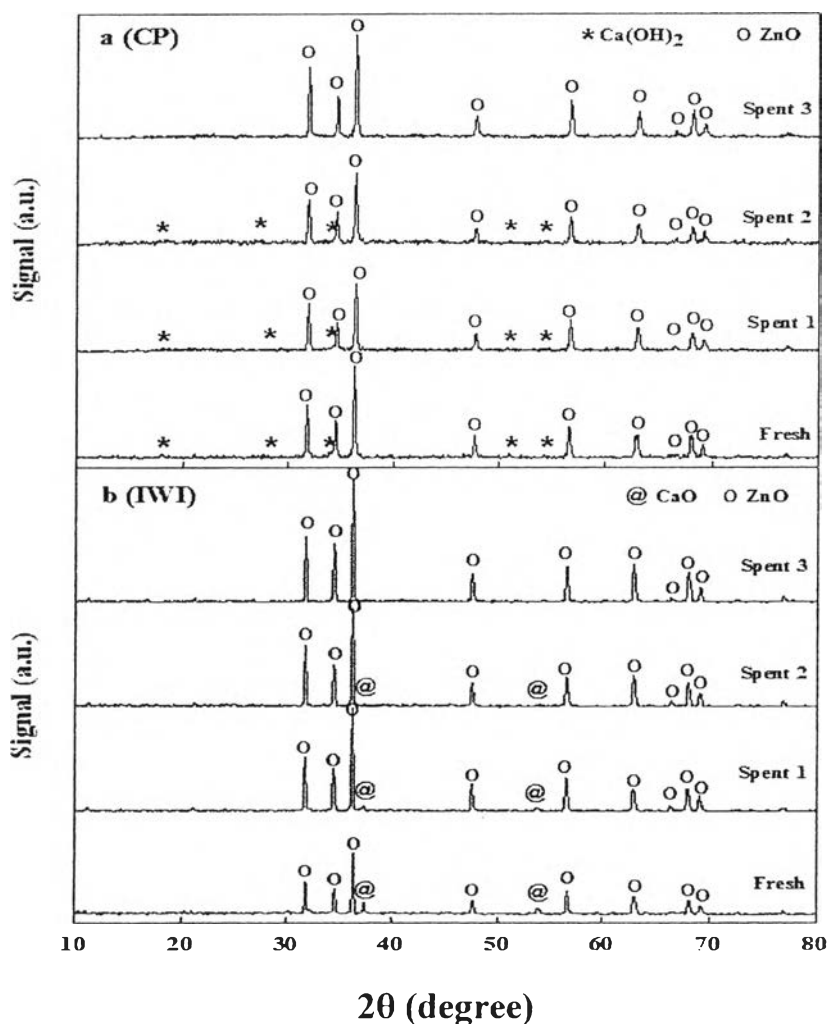


Figure 4.20 XRD patterns of Ca_1Zn_3 catalysts after durability testing: a) CP and b) IWI techniques.

Table 4.6 Mean crystallite sizes of the spent CaO–ZnO catalysts.

Samples	Calcination temperature (°C)	Crystallite size (nm)		
		CaO	Ca(OH) ₂	ZnO
<i>Co-precipitation</i>				
CaO-ZnO (1:3) Fresh catalyst	800 (6 h)	-	15.17	32.93
CaO-ZnO (1:3) Spent 1	800 (6 h)	-	30.01	29.07
CaO-ZnO (1:3) Spent 2	800 (6 h)	-	29.80	24.53
<i>Incipient wetness impregnation</i>				
CaO-ZnO (1:3) Fresh catalyst	900 (6 h)	36.85	-	37.63
CaO-ZnO (1:3) Spent 1	900 (6 h)	25.89	-	38.08
CaO-ZnO (1:3) Spent 2	900 (6 h)	38.56	-	26.73

4.3.2 X-ray Fluorescence Spectroscopy (XRF)

The chemical compositions of the durability testing of the catalysts were shown in Table 4.7. it was found that the %Ca of the spent catalysts decreased with increasing numbers of running time of reaction, as confirmed by XRD results.

Table 4.7 Comparison between the chemical compositions of the fresh and spent catalysts by using XRF measurement.

Samples	Calcination temperature (°C)	Element compositions (wt%)		Synthesized Ca/Zn	Expected Ca/Zn
		Ca	Zn		
<i>Co-precipitation</i>					
CaO–ZnO (1:3) Fresh catalyst	800 (6 h)	34.64	67.82	0.53	0.33
CaO–ZnO (1:3) Spent 1 ^a	800 (6 h)	32.18	67.82	0.47	0.33
CaO–ZnO (1:3) Spent 2 ^b	800 (6 h)	30.07	69.93	0.43	0.33
CaO–ZnO (1:3) Spent 3 ^c	800 (6 h)	28.06	71.94	0.39	0.33
<i>Incipient wetness impregnation</i>					
CaO–ZnO (1:3) Fresh	900 (6 h)	37.11	62.89	0.59	0.33
CaO–ZnO (1:3) Spent 1	900 (6 h)	35.18	64.82	0.54	0.33
CaO–ZnO (1:3) Spent 2	900 (6 h)	30.26	69.74	0.43	0.33
CaO–ZnO (1:3) Spent 3	900 (6 h)	24.82	75.18	0.33	0.33

^a1st running time of reaction^b2nd running time of reaction^c3rd running time of reactio

4.3.3 Scanning Electron Microscope (SEM)

SEM technique was used to determine the morphology of the fresh and spent catalysts, as imaged in Figure 4.21. It was found that the fresh CP catalyst (Figure 4.21a) shows the fine particles with the average particle diameter of $0.18\ \mu\text{m}$, while the fresh IWI catalyst (Figure 4.21c) shows the fine particles with the average particle diameter of $0.48\ \mu\text{m}$. However, the spent catalysts for both CP and IWI catalysts (Figure 4.21b and 4.21d) reveal a larger particle size due to their agglomeration, especially the spent IWI catalyst shows large decrease of surface area. It indicated that a decrease in the catalytic activity of CaO-ZnO catalyst in biodiesel production was obtained.

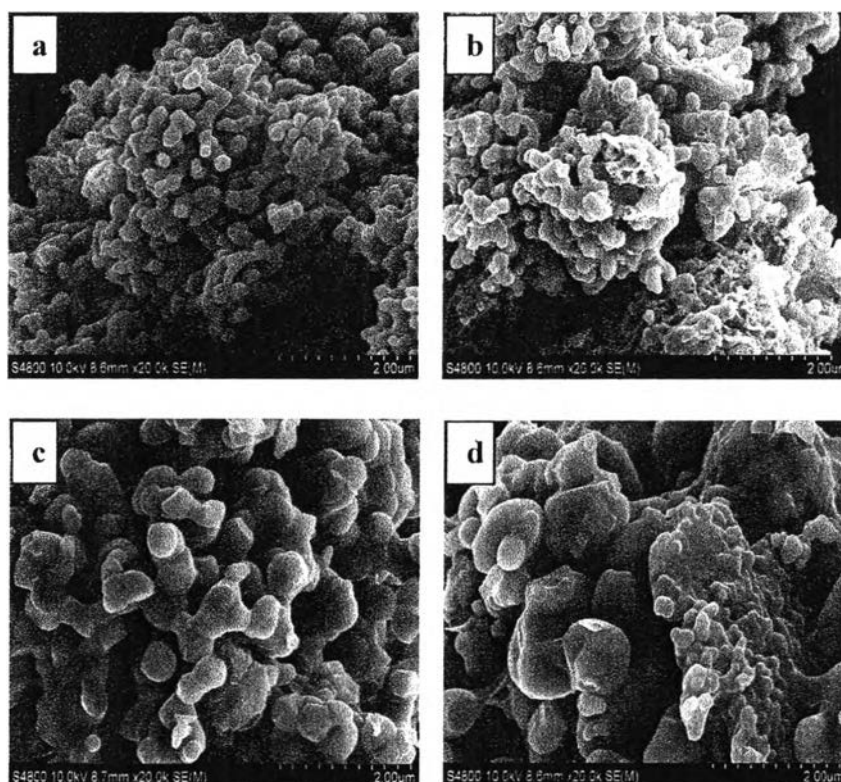


Figure 4.21 SEM images of a) fresh, b) spent CaO–ZnO catalysts prepared by CP method c) fresh, and d) spent CaO–ZnO catalysts prepared by IWI method.

4.3.4 Hammett Indicator

For the basic strength and basicity of the spent catalyst (Table 4.8), the results showed that the basic strength and basicity of the fresh catalysts were high in the range of $11 < H_0 < 15$ with the total basicity of 8.8040 and 6.8619 mmol/g for IWI and CP catalysts, respectively. However, basicity of spent 1 catalyst decreased dramatically for IWI catalyst and decreased slightly for basicity of spent 2 and spent 3 catalysts. For CP catalyst, basicity of spent catalysts decreased in constant rate for spent 1 to spent 3 catalysts. It indicates that the lacking of basic strength and basicity of the catalysts should occur from the leaching (or dissolved) of Ca substance into the product mixture and affected to the loss in catalytic activity. As evidenced by XRF, a decrease in %Ca of retested catalysts definitely confirmed this leaching phenomenon.

Table 4.8 Summarization of basic strength and basicity of the spent catalysts.

Sample		Basicity (mmol/g)				Total basicity (mmol/g)
		$7.2 < H_- < 9.8$	$9.8 < H_- < 11$	$11 < H_- < 15$	$15 < H_- < 18.4$	
<i>Incipient wetness impregnation (IWI)</i>						
CaO-ZnO (1:3)	Fresh	0.4314	0.6667	7.7059	-	8.8040
CaO-ZnO (1:3)	Spent 1	0.3220	0.2841	5.2273	-	5.8334
CaO-ZnO (1:3)	Spent 2	0.2655	0.2301	3.5752	-	4.0708
CaO-ZnO (1:3)	Spent 3	0.2510	0.1351	2.3745	-	2.7606
<i>Co-precipitation (CP)</i>						
CaO-ZnO (1:5)	Fresh	1.0476	0.2857	5.5286	-	6.8619
CaO-ZnO (1:3)	Spent 1	0.6714	0.2592	3.6142	-	4.5448
CaO-ZnO (1:1)	Spent 2	0.4305	0.2327	1.5460	-	2.2092
CaO-ZnO (3:1)	Spent 3	0.1174	0.1566	0.5871	-	0.8611

4.3.5 Fourier Transform Infrared Spectrophotometer (FT-IR)

The absorbances of fresh and spent catalysts for reusability study were scanned from 3500 cm^{-1} to 1000 cm^{-1} , as shown in Figure 4.22. In comparison to the fresh catalysts (CP and IWI), all spent catalysts obviously showed several characteristic functional groups of oil, such as C-H stretching (2924–2850 cm^{-1}), C=O stretching (1744 cm^{-1}), C-H bending (1654–1368 cm^{-1}), and C=C stretching (3014 cm^{-1}), which represented the contamination of biodiesel upon the catalyst's surface. Furthermore, these functional groups also tended to increase with running time, which could be referred to the accumulation of the amounts of biodiesel on the catalyst's surface.

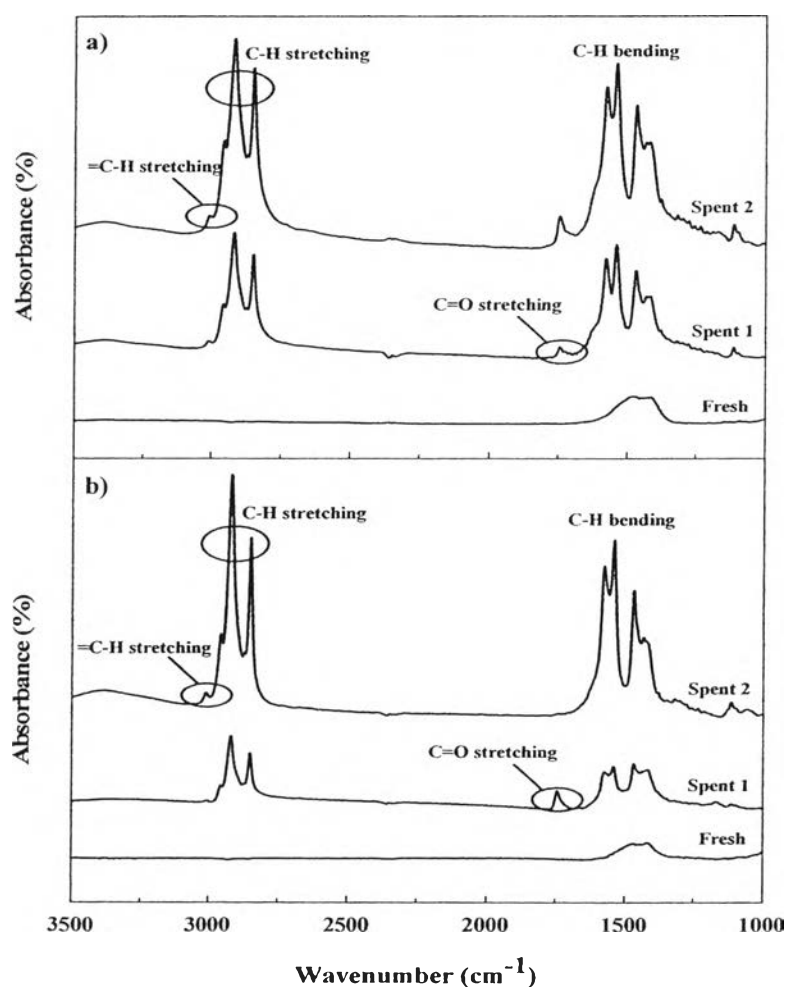


Figure 4.22 FTIR spectra of the spent Ca_1Zn_3 catalysts after durability testing: a) CP and b) IWI techniques.

4.4 Transesterification Reaction of Spent Catalyst

4.4.1 Effect of Catalyst Reusability

It is well-known in the field of catalyst that the life time of the prepared catalyst is defined as one of the most important criteria for the present commercialization. All of optimum conditions in the previous results—8 h of reaction time, 1:3 atomic ratio of Ca:Zn, and calcination temperature of 800 °C for CP catalyst and 900 °C for IWI catalyst —must be constantly fixed to investigate the catalyst reusability during the transesterification process at 60 °C. The reusability of the catalysts was applied for both IWI and CP techniques for comparison purposes. As shown in Figure 4.23, the IWI catalyst exhibited higher catalytic activity than the CP catalyst in the first run; however, the activity decreased gradually after the 2nd and 3rd runs. While catalytic activity of the CP catalyst has slightly decreased in the 2nd and 3rd runs. The reduction of FAME yield in the IWI and CP catalysts caused from lowering of active site, losing basicity, and decreasing of surface area, as confirmed by XRD, Hemmett indicators, and SEM.

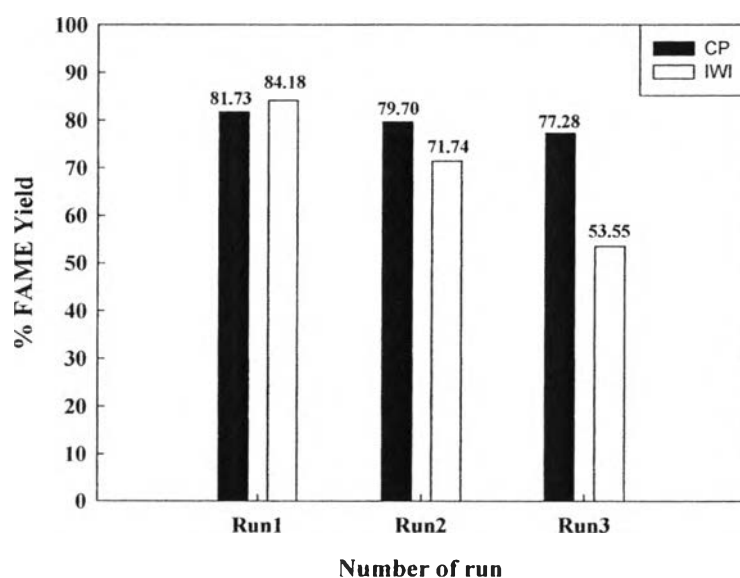


Figure 4.23 Durability of the CaO–ZnO catalysts on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed.