



CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of the catalysts

4.1.1 X-Ray Fluorescence

Table 4.1 Percentage of metal loading on the fresh and used catalysts

Catalyst	Fresh	Used
CaO/SBA-15	(CaO) 5.48 wt%	(CaO) 4.88 wt%
BaO/SBA-15	(BaO) 4.19 wt%	(BaO) 3.03 wt%
CaO/Al ₂ O ₃	(CaO) 5.33 wt%	(CaO) 3.98 wt%
BaO/Al ₂ O ₃	(BaO) 4.19 wt%	(BaO) 0.74 wt%
SILD CaO/Al ₂ O ₃	(CaO) 0.75 wt%	(CaO) 0.30 wt%
SILD BaO/Al ₂ O ₃	(BaO) 0.21 wt%	(BaO) 0.13 wt%

The metal composition of the fresh and spent catalysts were determined by X-ray Fluorescence, as illustrated in Table 4.1. For the fresh catalysts, when compared to the expected value of 4 wt%, it was found that there were some deviation of actual metal loading during the preparation, indicating that the impregnation technique might be difficult to control the metal contents on the catalyst surface. Nonetheless, the impregnated BaO catalysts seemed to provide the metal loading on support closely to the expected value. This might be related with the difference in metal-support interaction due to the nature of the metal and support properties. Consequently, the impregnation technique could perform better composition in BaO catalysts. Interestingly, the SILD catalysts showed the very low metal loading, suggesting that the metal could not be loaded easily with this technique. According to the used catalysts, it was obviously observed the dramatic decrease in the metal contents due to the fact that the metal leaching

during the reaction was occurred for either impregnation or SILD catalysts. As mentioned previously, it can be described that the problem of this leaching behavior could result in the rapid dropping of catalytic activities.

4.1.2 BET surface analysis

Table 4.2 Surface area and average pore diameter of the catalysts

Catalyst	Surface Area (m²/g)	Average Pore Diameter (nm)
Al ₂ O ₃	336	2.1
SBA-15	700	7.01
CaO/SBA-15	604	6.96
BaO/SBA-15	561	6.76
CaO/Al ₂ O ₃	145	10.8
BaO/Al ₂ O ₃	205	9.25
SILD CaO/Al ₂ O ₃	203	9.57
SILD BaO/Al ₂ O ₃	270	6.84

BET surface analysis results of the catalysts, and the supports were shown in Table 4.2. SBA-15 had the highest surface area, which was 700 m²/g, followed by CaO/SBA-15, BaO/SBA-15, Al₂O₃, SILD BaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and CaO/Al₂O₃, respectively. For average pore diameter, Al₂O₃ had the smallest average pore diameter, which was 2.1 nm, followed by BaO/SBA-15, SILD BaO/Al₂O₃, CaO/SBA-15, SBA-15, BaO/Al₂O₃, SILD CaO/Al₂O₃, and CaO/Al₂O₃, respectively. From these results, it showed that SBA-15 lost its surface area after being loaded by calcium oxide or barium oxide. As well as Al₂O₃, its surface area decreased after being loaded by calcium oxide or barium oxide by either impregnation or SILD method. In case of Al₂O₃, that effect might be caused by the increase of average pore diameter of the catalyst that occurred during the calcination step. But for SBA-15, it might be caused by

calcium oxide or barium oxide, that was loaded onto SBA-15. Because those metals would go into the pores of SBA-15 and then blocked up the pores, so the number of pores decreased.

4.2 Effect of Catalyst Type on the Etherification of Glycerol

The effect of catalyst type on the Etherification of glycerol was studied at 250°C under inert nitrogen atmosphere in the presence of 2 wt% of catalyst. Figure 4.1 illustrated the glycerol conversion for SBA-15, CaO/SBA-15, BaO/SBA-15, CaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃ as a function of reaction time. As expected, the conversion of glycerol increased along with reaction time and the investigated catalysts showed similar trends of glycerol conversion. The results suggested that there was no significant difference of glycerol conversion between SBA-15 supported catalysts, and Al₂O₃ supported catalysts and there was no major difference of glycerol conversion between impregnated catalysts and SILD catalysts as well. In addition, the final conversion of SBA-15, CaO/SBA-15, BaO/SBA-15, CaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃ are 2.5%, 12.9%, 13.5%, 12.7%, 13.3%, 14.0%, and 14.2%, respectively.

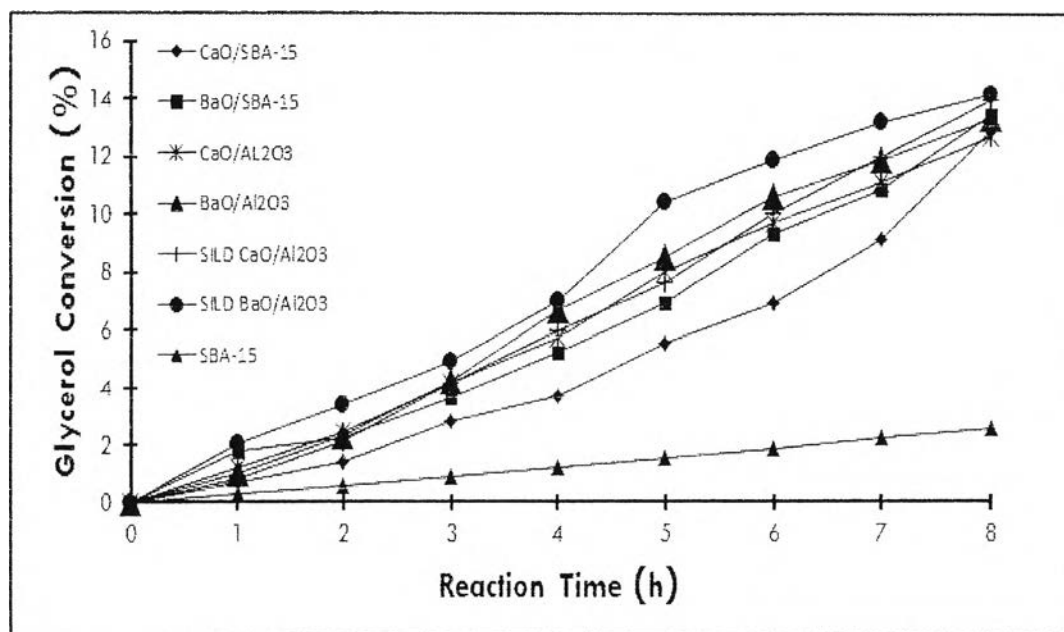


Figure 4.1 The glycerol conversion for SBA-15, CaO/SBA-15, BaO/SBA-15, CaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃ as a function of reaction time at 250 °C in the presence of 2 wt% of catalyst.

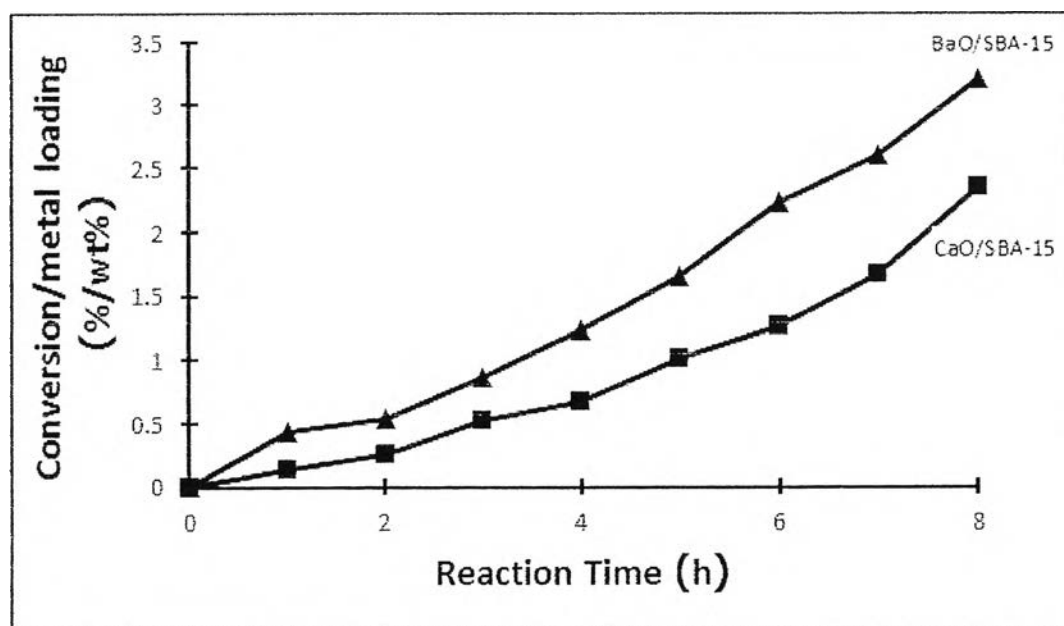


Figure 4.2 The glycerol conversion per percentage of metal loading for CaO/SBA-15 and BaO/SBA-15 as a function of reaction time at 250 °C in the presence of 2 wt% of catalyst.

Table 4.3 Surface area, percentage of metal loading and glycerol conversion of the catalysts

Catalyst	Surface Area (m ² /g)	Metal Loading (wt%)	Conversion (%)
CaO/SBA-15	604	5.48	12.9
BaO/SBA-15	561	4.19	13.5
CaO/Al ₂ O ₃	145	5.33	12.7
BaO/Al ₂ O ₃	205	4.19	13.3
SILD CaO/Al ₂ O ₃	203	0.75	14.0
SILD BaO/Al ₂ O ₃	270	0.21	14.2

From Table 4.3, SBA-15 supported catalysts had much more surface area than the others but the glycerol conversion were not higher. Figure 4.2, which was the combination result from Table 4.1 and Figure 4.1, was used to determine the actual activity of SBA-15 supported catalyst. Even though CaO/SBA-15 had more surface area than BaO/SBA-15 but it was still more active than CaO/SBA-15. From these results, it can be described that the activity of these catalysts does not depend upon only its surface area.

It can also be observed that percentage of metal loading does not conform to the glycerol conversion. Even SILD catalysts which had very low percentage of metal loading, they still had a higher glycerol conversion than impregnated catalysts. From this point, SILD technique seemed to be the key. Instead of randomly deposit metal onto a surface, that can cause the bulk-like phase, this technique provides the high dispersion of metal on surface. So SILD catalysts can show the higher glycerol conversion with the less percentage of metal loading when compared to impregnated catalysts.

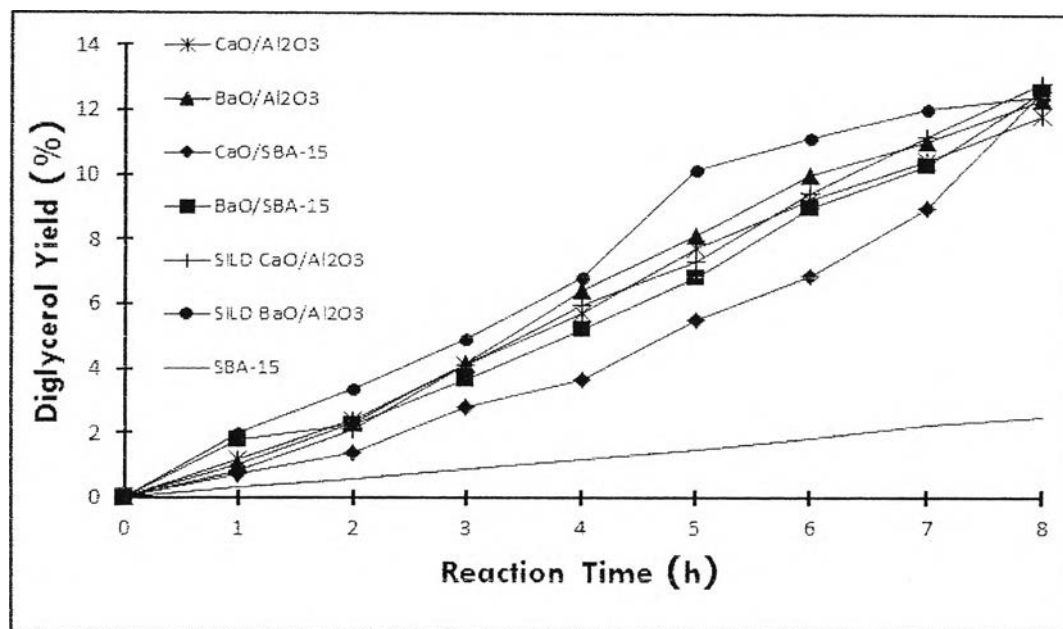


Figure 4.3 The diglycerol yield for SBA-15, CaO/SBA-15, BaO/SBA-15, CaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

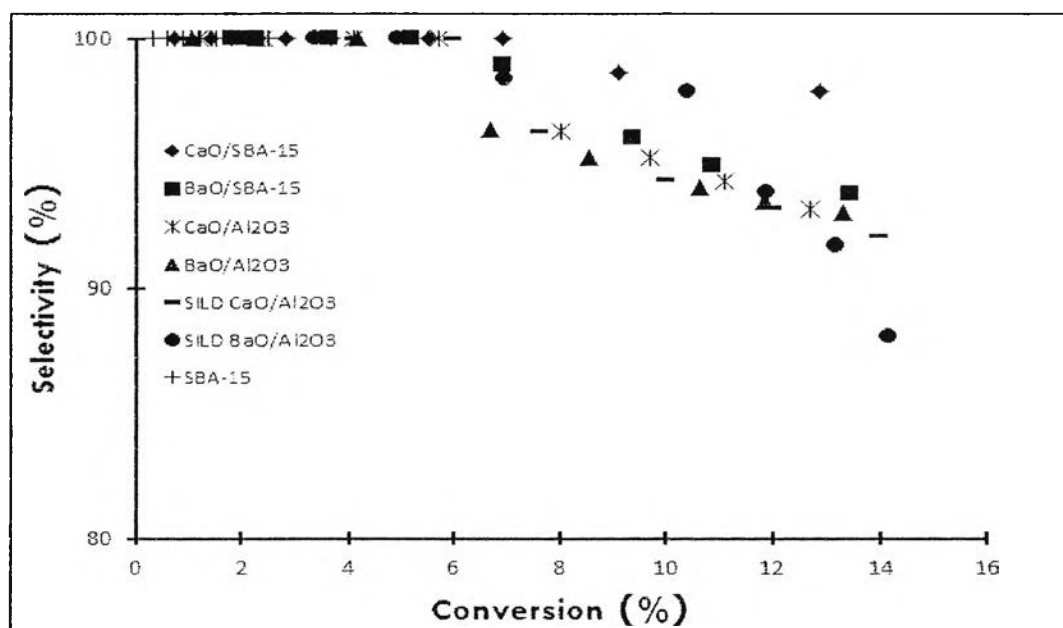


Figure 4.4 The diglycerol selectivity for SBA-15, CaO/SBA-15, BaO/SBA-15, CaO/Al₂O₃, BaO/Al₂O₃, SILD CaO/Al₂O₃, and SILD BaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

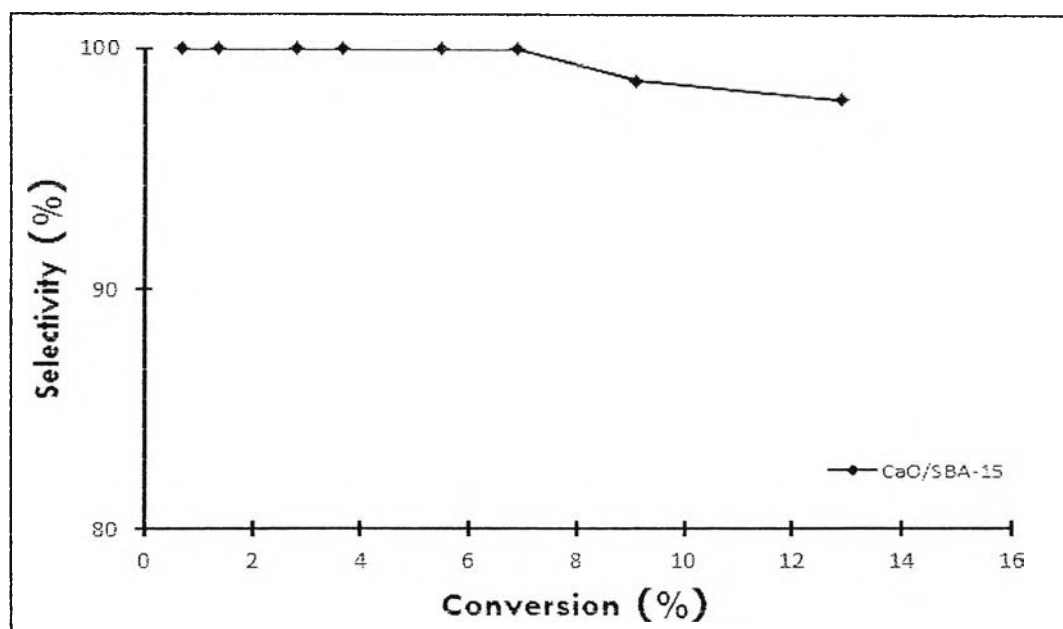


Figure 4.5 The diglycerol selectivity for CaO/SBA-15 as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

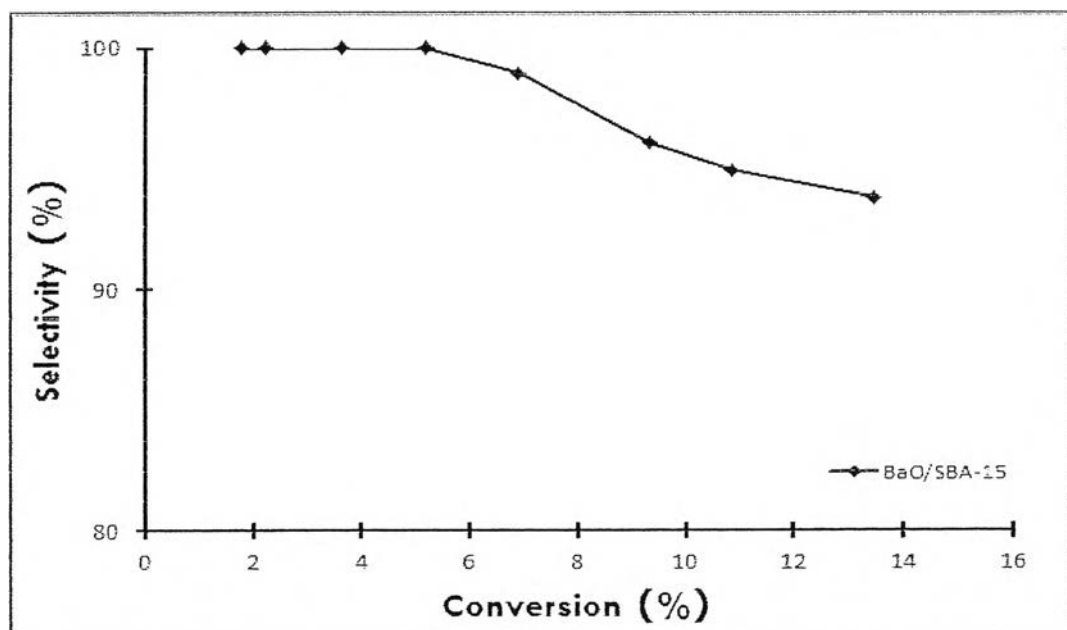


Figure 4.6 The diglycerol selectivity for BaO/SBA-15 as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

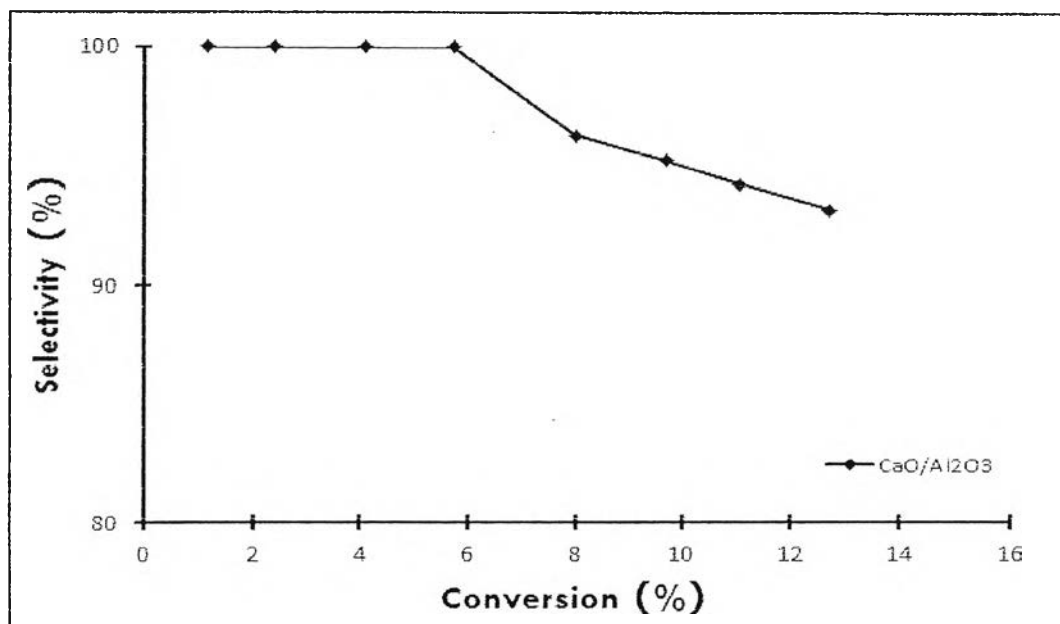


Figure 4.7 The diglycerol selectivity for CaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

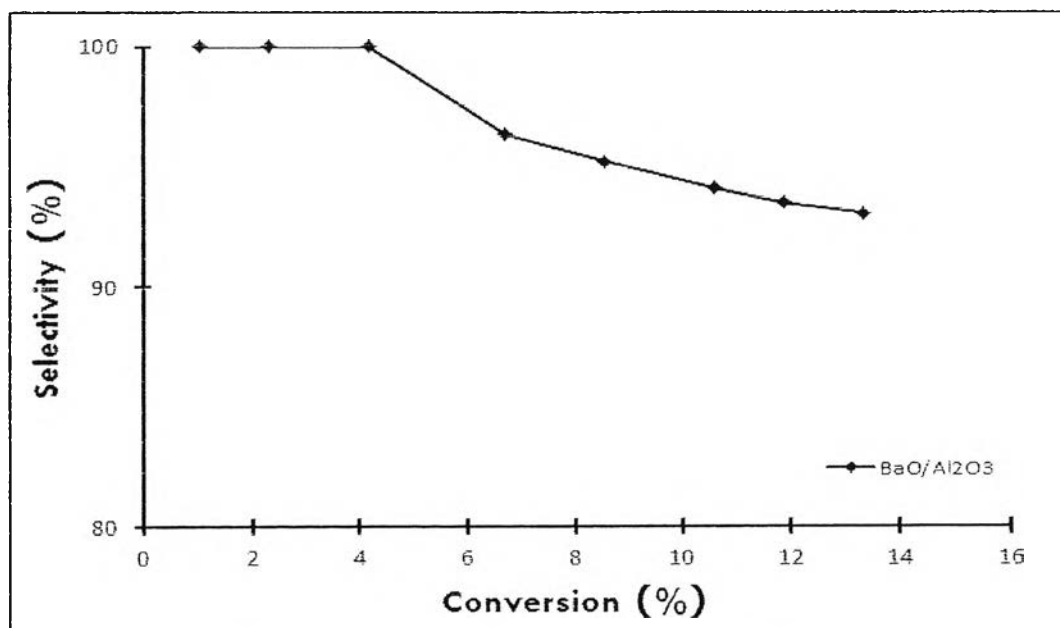


Figure 4.8 The diglycerol selectivity for BaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

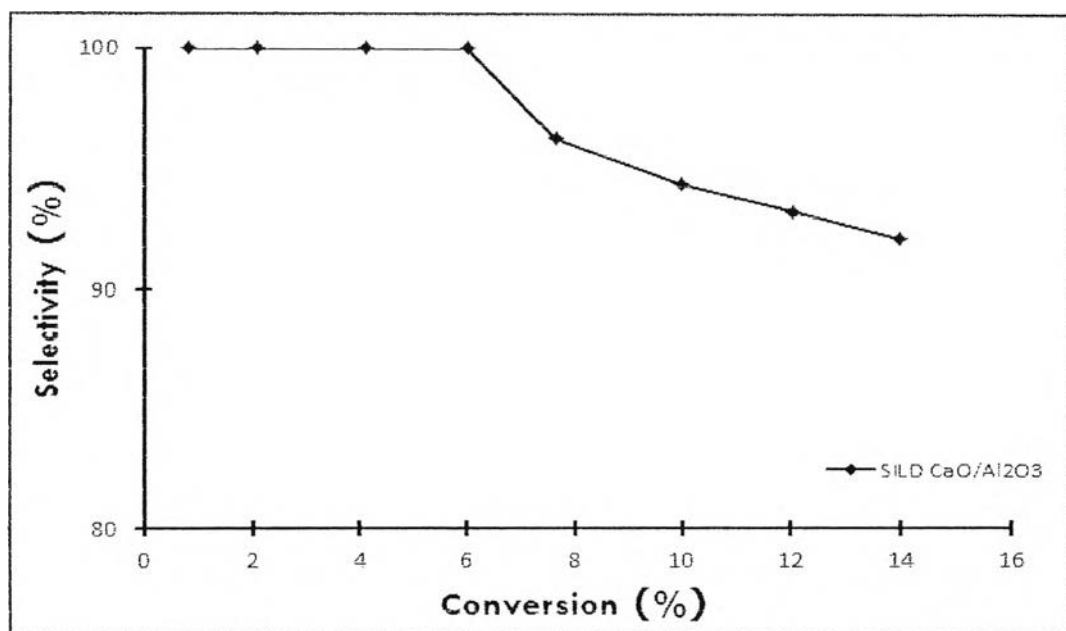


Figure 4.9 The diglycerol selectivity for SILD CaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

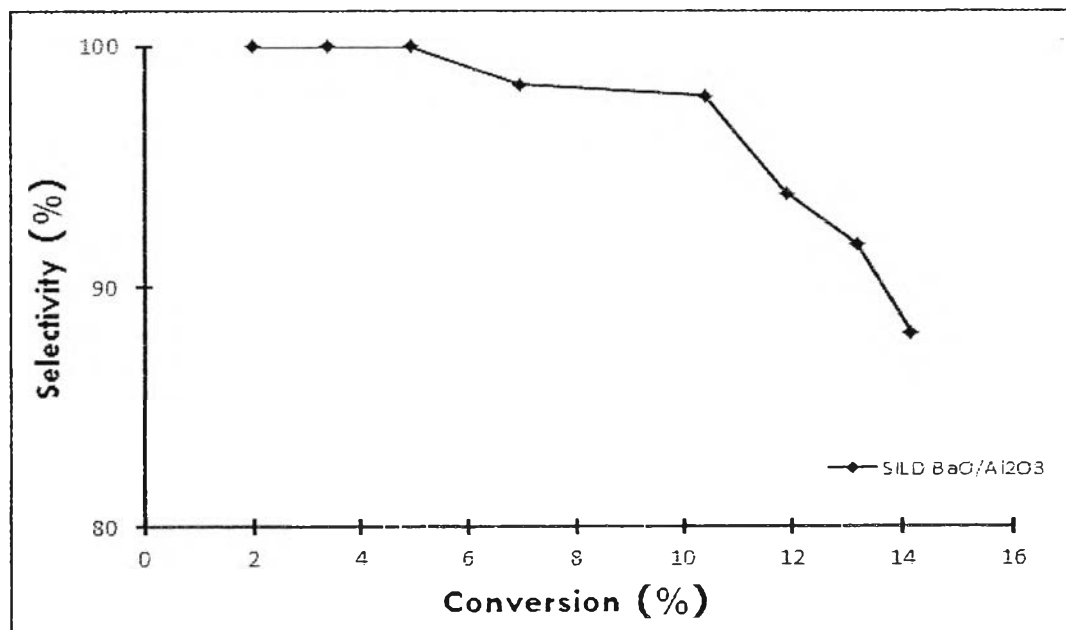


Figure 4.10 The diglycerol selectivity for SILD BaO/Al₂O₃ as a function of reaction time at 250°C in the presence of 2 wt% of catalyst.

At the beginning of reaction diglycerol is formed as the major product, while the higher polyglycerols start to govern at higher glycerol conversion. It can also be observed from Figure 4.3 that, diglycerol concentration of the catalysts includes Al_2O_3 and SBA-15 illustrate the related trends to glycerol conversion. And it is observed from Figure 4.4 that, the catalysts do not only catalyze glycerol to diglycerol, they also increase ability of glycerol to form triglycerol. This is due to the fact that diglycerol can further react with glycerol or diglycerol to form tri- and tetraglycerol and so on. Hence, the selectivity toward diglycerol is dropped if the reaction is extended. Figure 4.5 to Figure 4.10 summarize the selectivity of diglycerol for each catalyst applied. The diglycerol selectivity is defined as a ration of weight of diglycerol to weight of product (except remaining glycerol) according to Equation (4.1).

$$\text{Diglycerol Selectivity (wt \%)} = \frac{\text{Weight of diglycerol}}{\text{Weight of product}} \times 100 \quad (4.1)$$

Mesoporous supports used in this work may be effective at the beginning of the reaction. But when leaching problem occurs, mesoporous support will not have any effect on the reaction anymore. Because without the support, glycerol will have more chances to react with glycerol or diglycerol to generate polyglycerols, so diglycerol selectivity start to decrease.

It follows from Figure 4.7 that diglycerol selectivity of 100% is achieved only at low glycerol conversion up to around 6-7% and the selectivity declines with higher glycerol conversion. The different pore diameter of both SILD and impregnated catalysts might have some effects on Etherification of glycerol but only when metal leaching problem does not happen.