CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided into the following sections. Section 5.1 reports characterization of spinel type zinc gallate and zinc aluminate catalysts, Section 5.2 shown catalytic reaction at difference condition.

5.1 Characterization of zinc gallate and zinc aluminate

5.1.1 X-ray diffraction patterns (XRD)

The XRD patterns of the synthesized products with various Zn/Ga atomic ratios in the starting mixture obtained from glycothermal reaction at 300°C for 2 h are given in Figure 5.1. The spectra are similar with XRD pattern of $ZnGa_2O_4$ (spinel phase) [20], which were shown that spinel phase was formed without contamination with other phases such as ZnO and Ga_2O_3 at the starting atomic ratio Zn/Ga 0.5 and 0.25 (stoichiometric ratio). However, at starting Zn/Ga atomic ratios equal to 0.33 and 1.00 showed the peaks of contaminate phase of gallium oxide and zinc oxide, respectively.

For $ZnAl_2O_4$ the XRD patterns are shown in figure 5.2. The spectra are similar with XRD pattern of $ZnAl_2O_4$ (spinel phase) [20]. The sample with Zn/Al atomic ratio of 0.50 exhibited the completely similar XRD characteristic peak to the spinel phase. As for the samples with higher Zn/Al ratio (1.00) another peaks were observed which should be ascribed to the presence of an excess amount of ZnO and smaller. Zn/Al ratio (0.33) another peaks were observed which should be ascribed to the presence of an excess amount of Al_2O_3.

5.1.2 BET surface area

The total surface areas of catalysts were measured by BET single point method. Results are shown in Tables 5.1 and 5.2.

Table 5.1 Total surface area by BET single point method

Sample		BET Surface area (m^2/g)
$ZnGa_2O_4$		
	Zn/Ga 1.00	61.04
	Zn/Ga 0.50	41.33
	Zn/Ga 0.33	44.36
	Zn/Ga 0.25	47.42
$ZnAl_2O_4$		
	Zn/Al 1.00	82.06
	Zn/Al 0.50	113.06
	Zn/Al 0.33	144.45

Sangthonganothai, P. [20] found that the BET surface areas of zinc gallate and zinc aluminate synthesis by glycothermal method was higher than those synthesized by other methods.

Table 5.2 Total surface area by BET single point method and crystallize size*.

Sample	BET Surface area	d^b (nm)	d^c (nm)
$ZnGa_2O_4$			
Zn/Ga 1.00	67.69	14.42	14.33
Zn/Ga 0.50	52.27	18.13	18.33
Zn/Ga 0.33	76.51	10.80	10.67
$ZnAl_2O_4$			
Zn/Al 1.00	86.72	12.36	12.67
Zn/Al 0.50	155.68	9.81	9.67
Zn/Al 0.33	156.35	7.98	7.99

* referred to Sangthonganothai, P [20].

[b] Crystallite size of products calculated from Scherer equation using KCl as an internal standard.

[c] Crystallite size of products from TEM photograph.

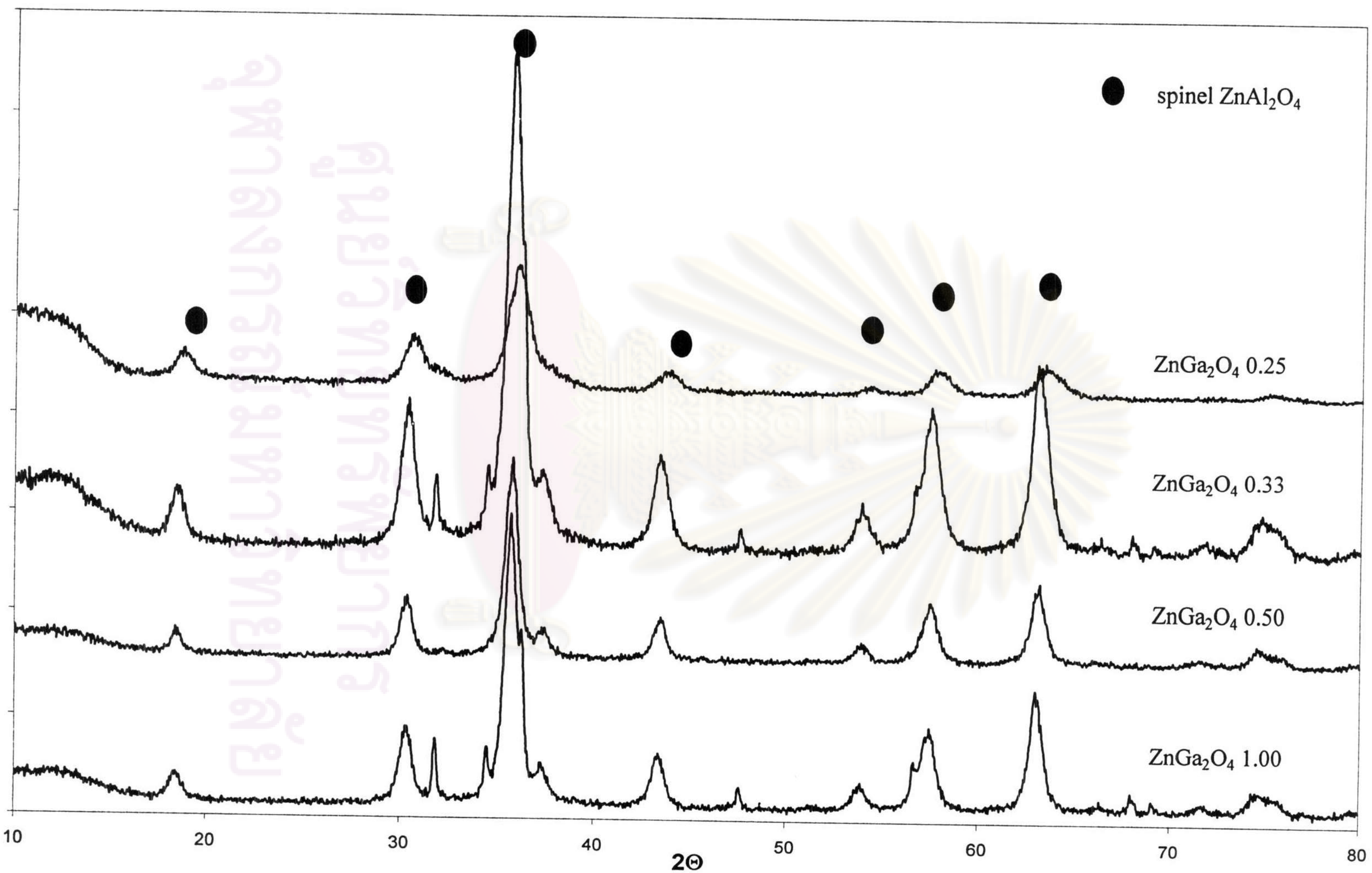

Figure 5.1 X-ray Diffraction pattern of zinc gallate ($ZnGa_2O_4$)

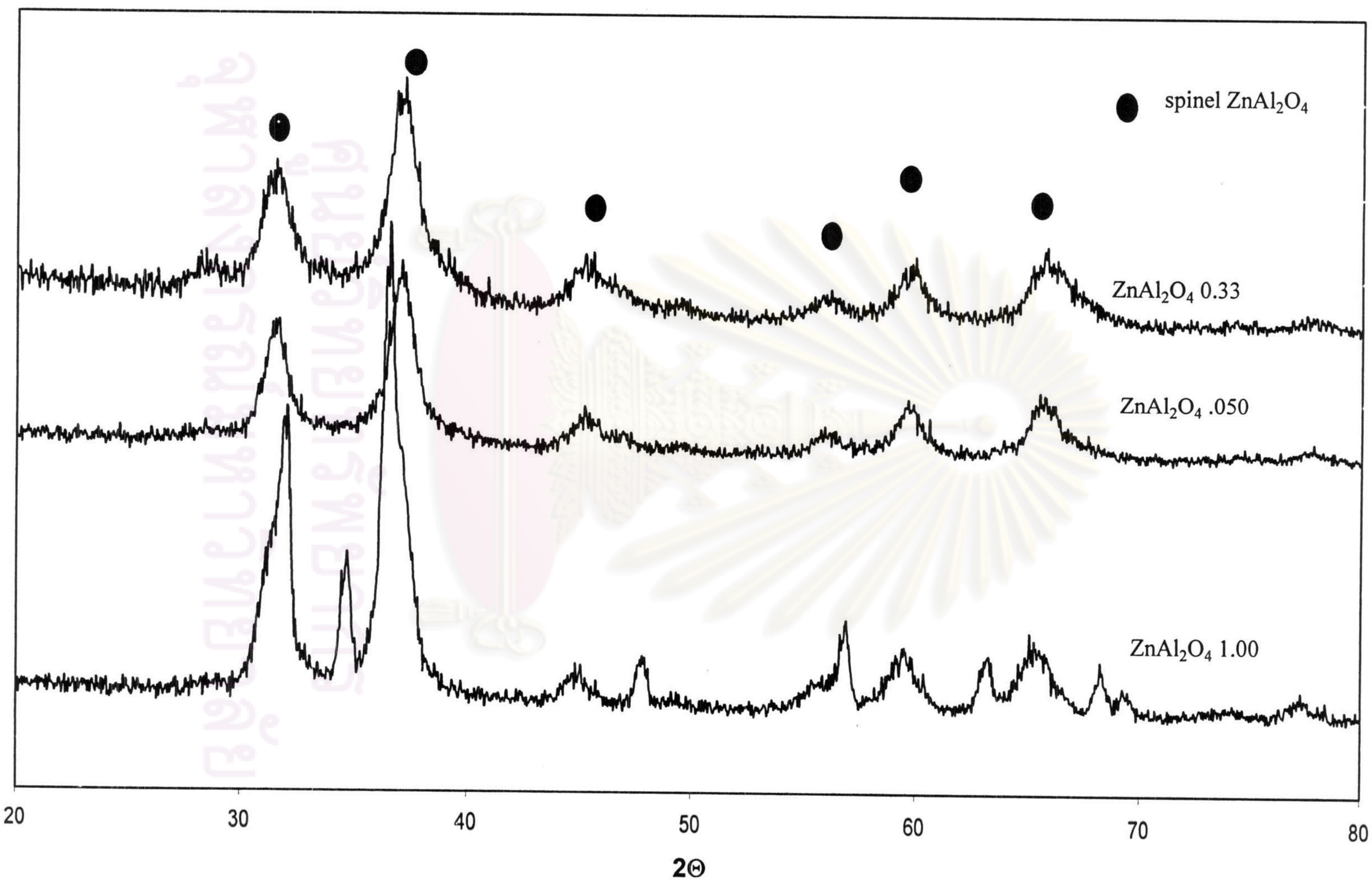

Figure 5.2 X-ray Diffraction pattern of zinc aluminate ($ZnAl_2O_4$)

5.2 Catalytic reaction

The catalytic property of the zinc gallte and zinc aluminate catalyst is investigated by using the oxidative dehydrogenation reaction as the test reaction. Catalyst pretreated in inert gas can be selected the better performance for oxidative dehydrogenation [30]. For all experimental, the major product was propylene along with small amounts of ethane, ethylene, and methane.

5.2.1 Catalyst test for zinc gallate ($ZnGa_2O_4$)

The catalytic property of $ZnGa_2O_4$ catalyst is presented in figure 5.3 and figure 5.4. The propane conversion increases slightly with increasing temperatures from 400°C to 450°C, when the reaction temperature is higher than 450°C, the propane conversion increases rapidly, while the selectivity to propylene decreases rapidly with increased temperatures from 400 °C to 500 °C, then the reaction is higher than 500 °C, propylene selectivity is decreases slightly. The cause of the reduction in propylene selectivity at high reaction temperatures is due to the further oxidation of propylene to combustion products. For $ZnGa_2O_4$ atomic ratio 0.50, at reaction temperatures 500°C-600°C propane selectivity increases slightly to 20%.

Propylene yield of $ZnGa_2O_4$ is presented in Figure 5.5, the curve of yield of $ZnGa_2O_4$ atomic ratios 0.33 and 0.25 is similar, and the yield is about 5-8 %. Propylene yield increases slightly with increasing reaction temperatures from 400°C to 500°C for $ZnGa_2O_4$ atomic ratio 0.50 and for 400°C to 550°C for $ZnGa_2O_4$ atomic ratio 1.00. Then the reaction temperatures higher than 500°C and 550°C propylene yield increase rapidly to 13 % and 17 %, respectively. For $ZnGa_2O_4$ atomic ratio 0.50 propylene yields increase at reaction temperatures 500°C-600°C.

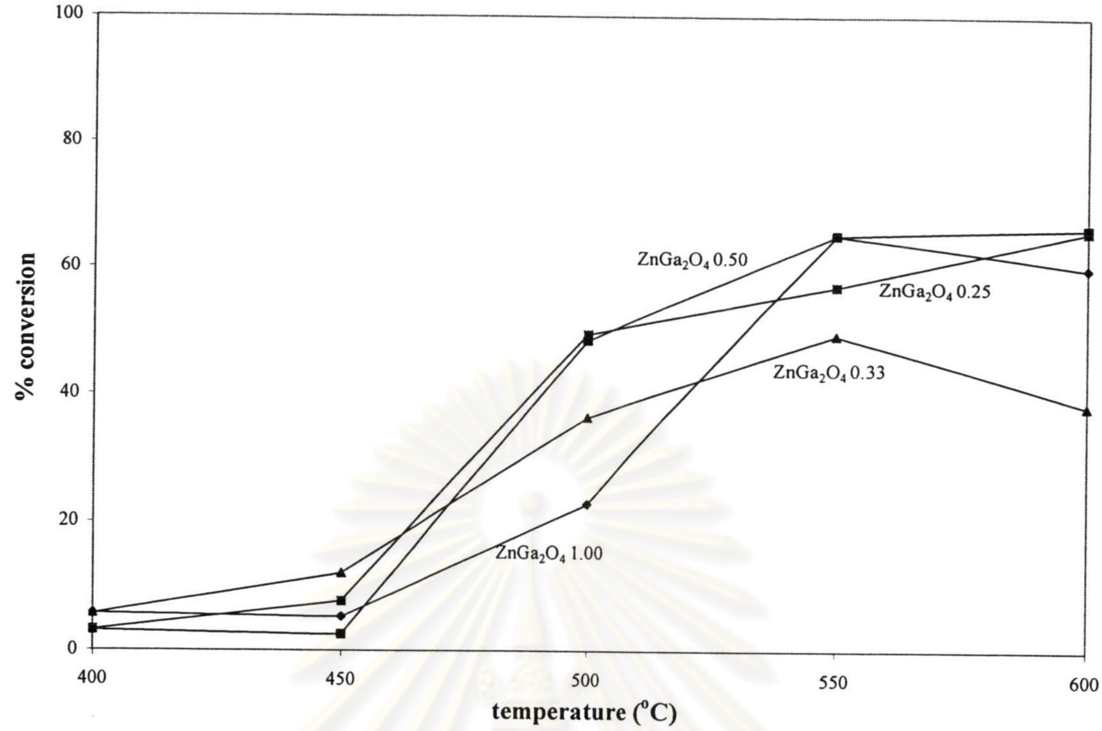

Figure 5.3 Propane conversion of oxidative dehydrogenation of propane on $ZnGa_2O_4$ catalysts.

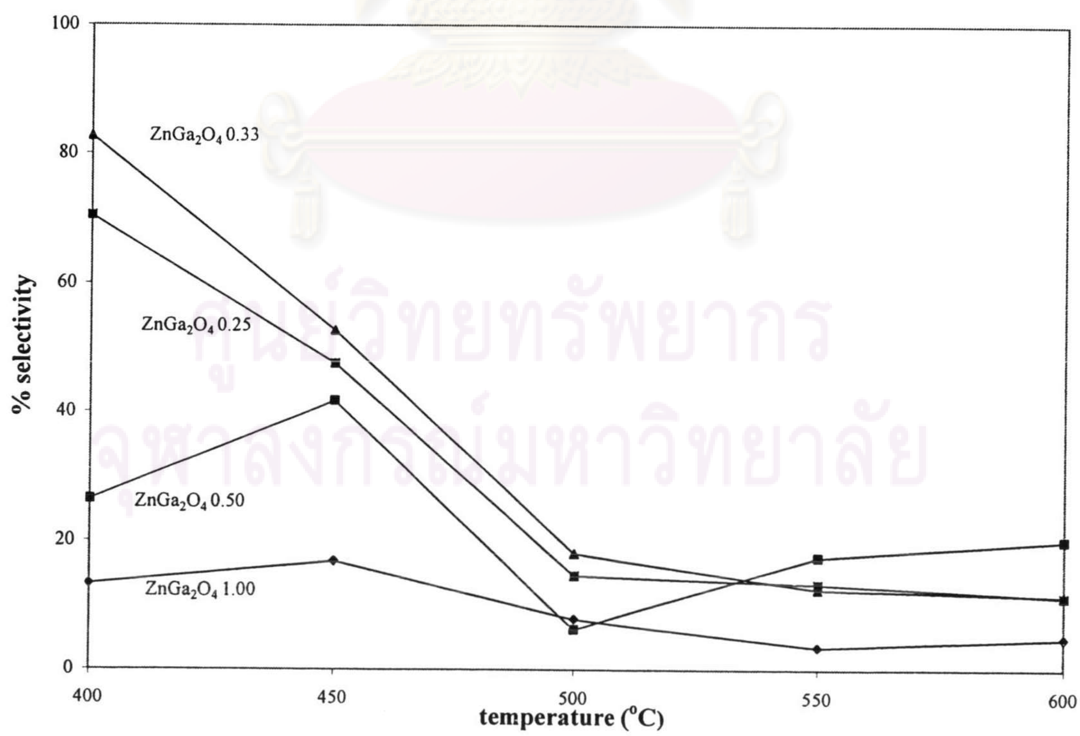

Figure 5.4 Propane selectivity of oxidative dehydrogenation of propane on $ZnGa_2O_4$ catalysts.

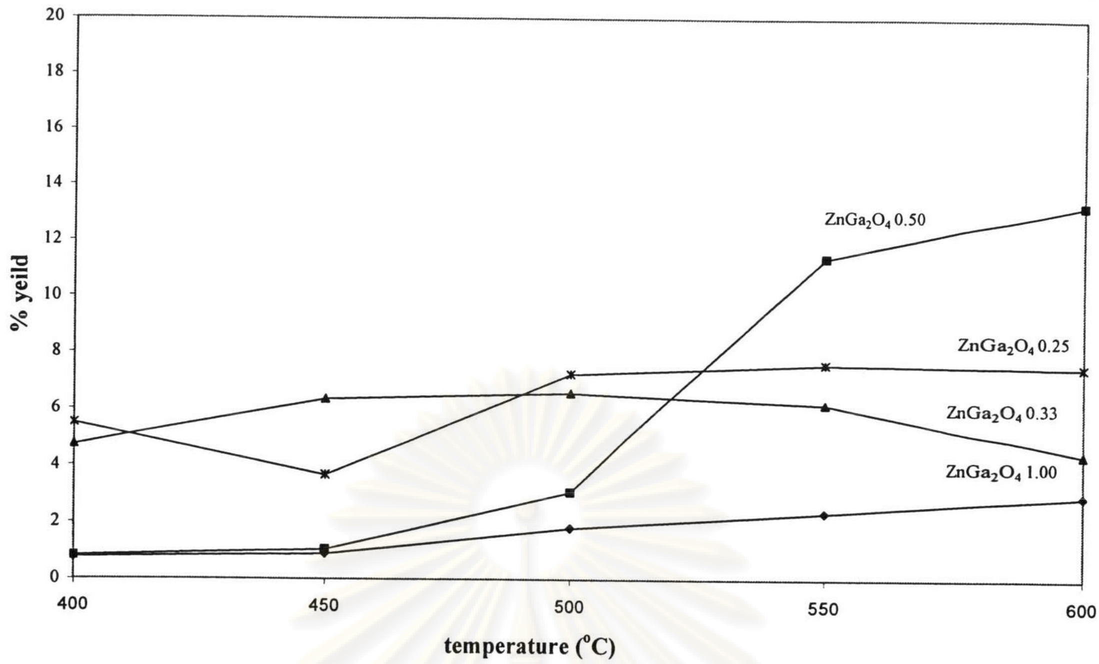

Figure 5.5 Propane yield of oxidative dehydrogenation of propane on $ZnGa_2O_4$ catalysts.

Effect of $ZnGa_2O_4$ composition

Sangthonganothai, P [20], prepare $ZnGa_2O_4$ with vary composition of $ZnGa_2O_4$ by vary the Ga contents at Zn/Ga atomic ratio of 1.00, 0.50 and 0.33, at any composition of $ZnGa_2O_4$ have spinel structure with atomic ratios of Zn/Ga respect to the amounts of reactant in preparation step.

Catalyst composition has effect on oxidative dehydrogenation of propane, at low conversion change period (temperatures between 400°C-500°C); at temperature 400 °C propane conversion is not different. The different propane conversion can be seen when the temperatures are higher than 450°C, at reaction temperature 500°C maximum propane conversion can be achieved at $ZnGa_2O_4$ atomic ratios of 0.25 and 0.50 and at higher reaction temperature $ZnGa_2O_4$ atomic ratios 0.50 and 0.25 were maximum propane conversion, too. Propylene selectivity $ZnGa_2O_4$ atomic ratio 0.33 is maximum propylene selectivity and $ZnGa_2O_4$ atomic ratio 1.00 have minimum propylene selectivity with reaction temperature from 400°C to 500°C. The activity of catalyst can considered from propylene yield (figure 5.5) and reaction temperature, the operation need low temperature to decreases operation cost. At high reaction temperature above 550°, $ZnGa_2O_4$ atomic ratio 0.50 have highest propylene yield but they have high energy consume. Temperature between 400°C-500°C, $ZnGa_2O_4$ atomic ratio 0.33 can be should, the smaller amount of Ga used in preparation step than $ZnGa_2O_4$ atomic ratio 0.25, nearly propylene yields.

The compositions of $ZnGa_2O_4$ have effect on oxidative dehydrogenation of propane to propylene, at reaction temperatures between 400°C-500°C they have high effect on propylene selectivity, $ZnGa_2O_4$ atomic ratio 0.33 has Ga_2O_3 phase and $ZnGa_2O_4$ atomic ratio 1.00 has ZnO phase in the structure or on surface (Zn/Ga atomic ratio 0.50 has only complete spinel phase). It is believed that Ga increases propylene selectivity. When increasing Ga in preparation step (increases Ga in structure or surface) more than Zn/Ga atomic raio 0.33, propylene selectivity are not increases, so Ga contents in structure or surface that are suitable can be effect on propylene selectivity(make a good propylene selectivity). $ZnGa_2O_4$ atomic ratio 1.00 have excess Zn to formation of ZnO, they decreases propylene selectivity.

The $ZnGa_2O_4$ atomic ratio 0.33 has the highest selectivity, there are speculated that Ga cations in spinel structure increase selectivity, while catalysts have spinel structure, so $ZnGa_2O_4$ atomic ratio 0.25 will have highest selectivity. From catalysts testing, found that the selectivity less than $ZnGa_2O_4$ atomic ratio 0.33, it should be occurred by the loss of Ga_2O_3 phase in $ZnGa_2O_4$ atomic ratio 0.25 or may be loss spinel structure in $ZnGa_2O_4$ atomic ratio 0.25 and found that ZnO phase in spinel structure of $ZnGa_2O_4$ decrease selectivity, it suggested that Ga-O is the active center for oxidative dehydrogenation of propane to propylene.

From the results, at reaction temperatures 525°C-600°C $ZnGa_2O_4$ atomic ratio 0.50 has highest yield (7-12 %) when compare with all compositions.

5.2.2 Catalyst test for zinc aluminate ($ZnAl_2O_4$)

The catalytic property of $ZnAl_2O_4$ catalysts is presented in Figures 5.6 and 5.7, the propane conversion increases slightly with increasing temperatures from 400 °C to 500°C, when the reaction temperature is higher than 500°C, propane conversion increases rapidly, while the selectivity to propylene decreases rapidly with increasing reaction temperatures from 400 °C to 600 °C. The cause of the reduction in propylene selectivity at high reaction temperatures is due to the further oxidation of propylene to combustion products.

The propylene yield of $ZnAl_2O_4$ are presented in Figure 5.8, propylene yield of $ZnAl_2O_4$ catalysts increases slightly with increasing reaction temperatures from 400°C to 600 °C for all catalysts atomic ratio. Propylene yield of $ZnAl_2O_4$ atomic ratio 0.33 is maximum and $ZnAl_2O_4$ atomic ratio 1.00 is minimum, propylene yield at any composition are similar at low temperature (400°C-500°C). When reaction temperatures higher than 500°C the different propylene yields appear.

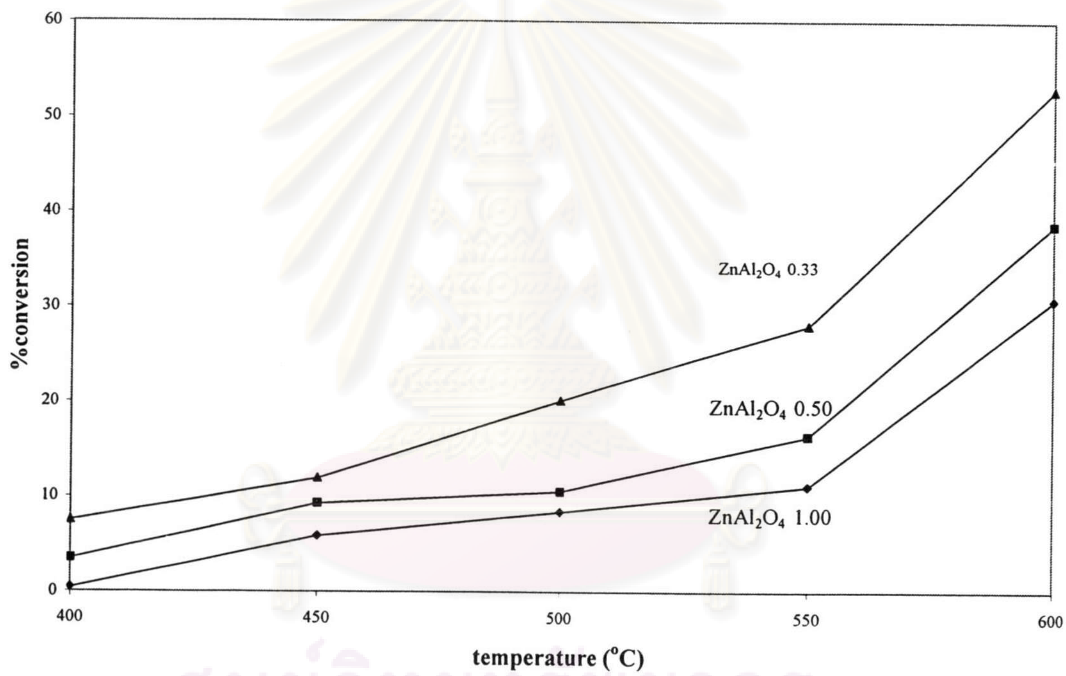

Figure 5.6 Propane conversion of oxidative dehydrogenation of propane on $ZnAl_2O_4$ catalysts

Effect of $ZnAl_2O_4$ composition

The compositions of $ZnAl_2O_4$ catalysts were effect on oxidative dehydrogenation of propane, at low temperature between 400°C-500°C, propane conversion are not different. Activity of $ZnAl_2O_4$ catalysts have been shown by propylene yield (Figure 5.8) and reaction temperatures. Propylene yield of every Zn/Al atomic ratio increases slightly with increasing reaction temperatures. $ZnAl_2O_4$

atomic ratio 0.33 have highest yield at any reaction temperature, and propylene yield of $ZnAl_2O_4$ atomic ratio 0.33 > $ZnAl_2O_4$ atomic ratio 0.50 > $ZnAl_2O_4$ atomic ratio 1.00. Between temperature 400°C-500°C, propylene selectivity of $ZnAl_2O_4$ atomic ratios (Zn/Al) 0.50 > $ZnAl_2O_4$ atomic ratio 0.33 > $ZnAl_2O_4$ atomic ratio 1.00. The excess Al in catalyst ($ZnAl_2O_4$ atomic ratio 0.33) has the formation of Al_2O_3 in the structure or surface, propylene selectivity decreases about 20%. The Al contents that is suitable for this case is $ZnAl_2O_4$ atomic ratio 0.50. The excess of Zn in catalyst ($ZnAl_2O_4$ atomic ratio 1.00) have the formation of ZnO phase in the structure or surface, propylene selectivity are smaller than propylene selectivity of $ZnAl_2O_4$ atomic ratio 0.33 about 15%.

From the results, at reaction temperatures 475°C-525°C $ZnAl_2O_4$ atomic ratio 0.5 has highest yield (4.5-5.5%) when compare with all compositions. The excess Zn and Al in catalysts were decreases propylene selectivity and propylene selectivity of excess Al is higher than excess Zn.

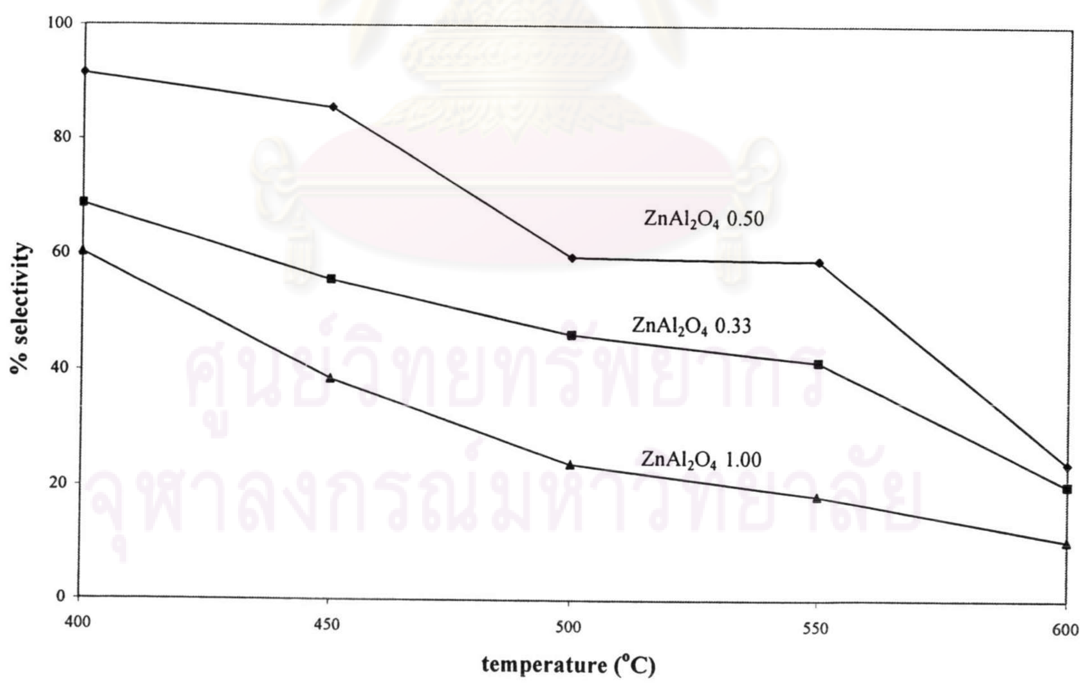

Figure 5.7 Propane selectivity of oxidative dehydrogenation of propane on $ZnAl_2O_4$ catalysts.

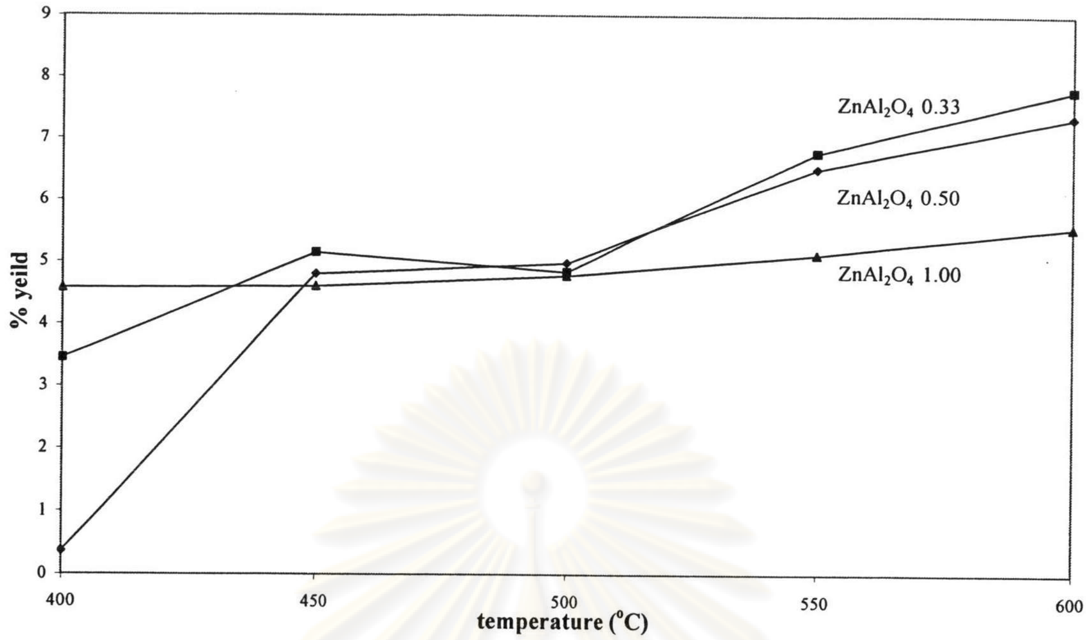

Figure 5.8 Propane yield of oxidative dehydrogenation of propane on $ZnAl_2O_4$ catalysts

The $ZnAl_2O_4$ atomic ratio 0.5, with complete spinel structure has highest selectivity. For $ZnAl_2O_4$ atomic ratios 1.00 and 0.33 the selectivity decrease. It suggest that ZnO phase in spinel decrease selectivity in oxidative dehydrogenation, it probably affects of chemisorptions of oxygen ions on ZnO at high temperatures, ZnO will be loss oxygen ions or not absorb oxygen ions (n-type of chemisorption on oxides surface will be loss oxygen when increase temperatures [34]).

The increasing of Al contents or Al_2O_3 phase in spinel structure will decrease selectivity of oxidative dehydrogenation, so the excess Al_2O_3 phase are importance in this system, the effect of Al_2O_3 phases in spinel on oxidative dehydrogenation, from the properties of Al_2O_3 are amphotoric it may be loss of absorb oxygen. From catalytic test results it Al_2O_3 phase show the loss of adsorb oxygen in oxidative dehydrogenation because absorb oxygen are important for the selectivity. It suggests that Al_2O_3 phase in $ZnAl_2O_4$ spinel decrease selectivity in oxidative dehydrogenation of propane to propylene.

Compare catalytic performance of $ZnGa_2O_4$ and $ZnAl_2O_4$ catalysts

At reaction temperature 400°C-450°C, propane conversion of $ZnGa_2O_4$ and $ZnAl_2O_4$ are similar. When reaction temperatures are higher than 450°C, a difference in propane conversion are appeared, propane conversion of $ZnGa_2O_4$ is higher than $ZnAl_2O_4$, while propylene selectivity of $ZnAl_2O_4$ is higher than $ZnGa_2O_4$. At reaction temperatures between 400°C and 500°C, $ZnAl_2O_4$ have higher propylene selectivity than that $ZnGa_2O_4$. Propylene yield of $ZnAl_2O_4$ were similar yield at any reaction temperature and catalysts atomic ratio. Propylene yield of $ZnGa_2O_4$ have two difference, first $ZnGa_2O_4$ atomic ratio 0.50 and 1.00, at reaction temperatures 400°C-500°C have small propylene yield, and then $ZnGa_2O_4$ atomic ratios 0.33 and 0.25 propylene have similar and they have maximum yield of the reaction.

The catalytic performance for catalyst having atomic ratio 0.5 and 1.00, at reaction temperatures 400°C-500°C performances of $ZnAl_2O_4$ were better then $ZnGa_2O_4$. Thus, reaction temperatures higher than 500°C catalytic performances of $ZnGa_2O_4$ were better than $ZnAl_2O_4$. For catalyst atomic ratio 0.33, catalytic performance of $ZnGa_2O_4$ is better than $ZnAl_2O_4$ at low reaction temperatures, when reaction temperatures higher than 500°C catalytic performance of $ZnAl_2O_4$ were better than $ZnGa_2O_4$.

From sum of the results, found that at reaction temperatures 525°C-550°C $ZnGa_2O_4$ atomic ratios 0.50 has highest performance.

The lower oxygen cation's bond energy in catalytic system or in the structure of spinel has low selectivity for oxidative dehydrogenation of propane to propylene [13]. For $ZnGa_2O_4$ and $ZnAl_2O_4$ they have the different coordination of oxygen surrounding in oxide, Ga-O and Al-O, to predict oxygen bond energy, Ga-O will have oxygen bond energy less than Al-O when compare with electro-negativity of Ga and Al atom. From the catalyst testing $ZnAl_2O_4$ has higher selectivity than $ZnGa_2O_4$, they supported to that Ga have lower oxygen cation's bond energy.