

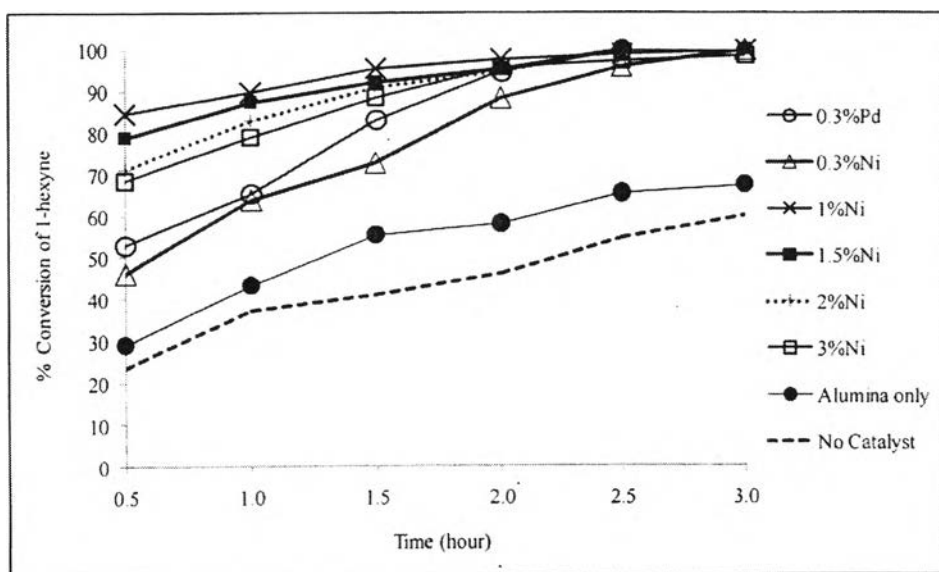
## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Catalytic Activity

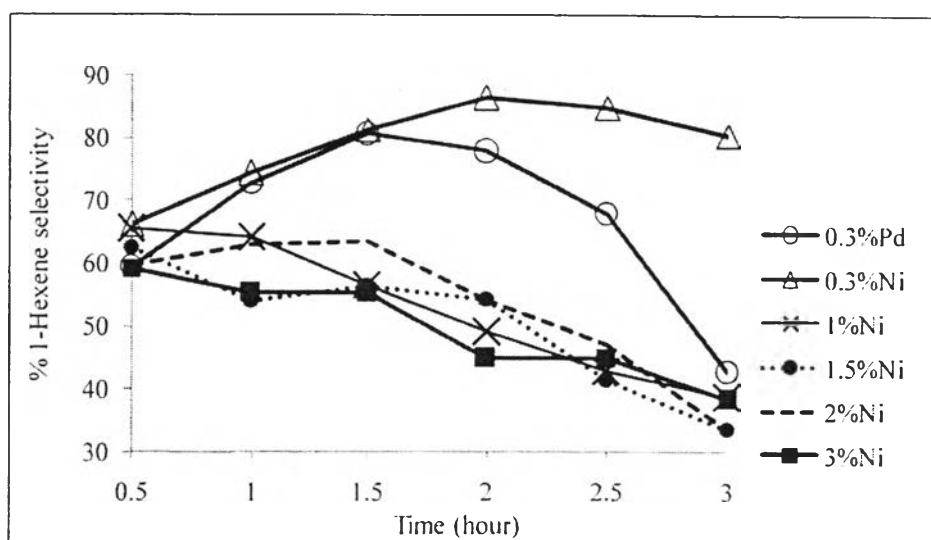
##### 4.1.1 Pd and Ni Supported on Alumina

The activity of Pd and Ni monometallic with various Ni loading supported on alumina catalysts were investigated for the hydrogenation of 1-hexyne at 1.5 bar and 40 °C. Fig. 4.1 shows the catalytic activity of 1-hexyne hydrogenation by 0.3%Pd/Al<sub>2</sub>O<sub>3</sub>, 0.3%Ni/Al<sub>2</sub>O<sub>3</sub>, 1%Ni/Al<sub>2</sub>O<sub>3</sub>, 1.5%Ni/Al<sub>2</sub>O<sub>3</sub>, 2%Ni/Al<sub>2</sub>O<sub>3</sub>, 3%Ni/Al<sub>2</sub>O<sub>3</sub>, alumina, and no catalyst. It is found that 1%Ni/Al<sub>2</sub>O<sub>3</sub> provides higher activity than other prepared catalysts. If Ni loading is higher than 1%, the activity drops significantly probably due to the decrease of active site. For the same level of metal loading, 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> exhibits higher activity than 0.3%Ni/Al<sub>2</sub>O<sub>3</sub>, while alumina and no catalyst show relatively low activity.



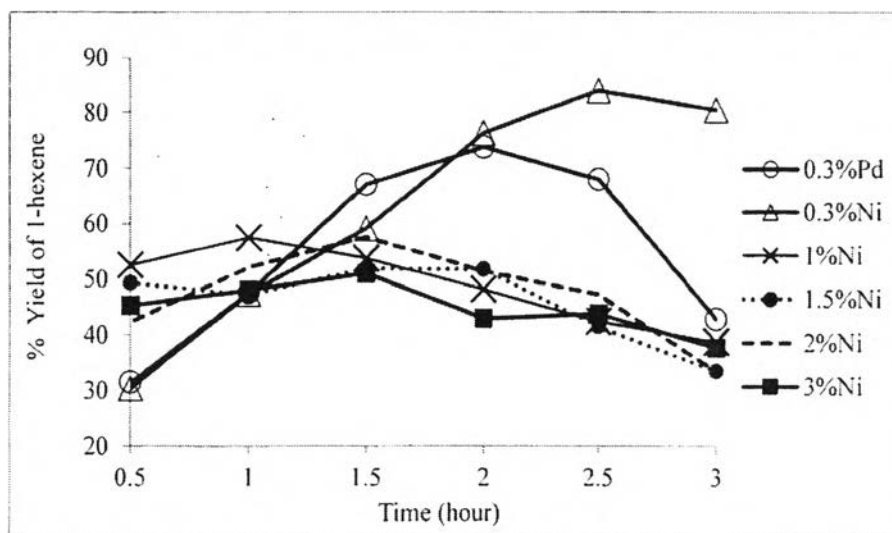
**Figure 4.1** 1-Hexyne total conversions (%) as a function of time for Pd/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.

Fig. 4.2 illustrates 1-hexene selectivity as a function of reaction time for Pd and Ni on alumina catalysts. Low load 0.3wt% of Pd and Ni exhibits the increase of 1-hexene selectivity with reaction time. However 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> exhibits 1-hexene selectivity drops after 1.5 hour, while 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> shows the decrease of 1-hexene selectivity after 2 hours. Interestingly, 1-hexene selectivity is significant decreased when 1%, 1.5%, 2% and 3%Ni/Al<sub>2</sub>O<sub>3</sub> is used. possibly due to high activity toward 1-hexene hydrogenation to *n*-hexane. It can be observed that 0.3%Ni exhibits the highest 1-hexene selectivity.



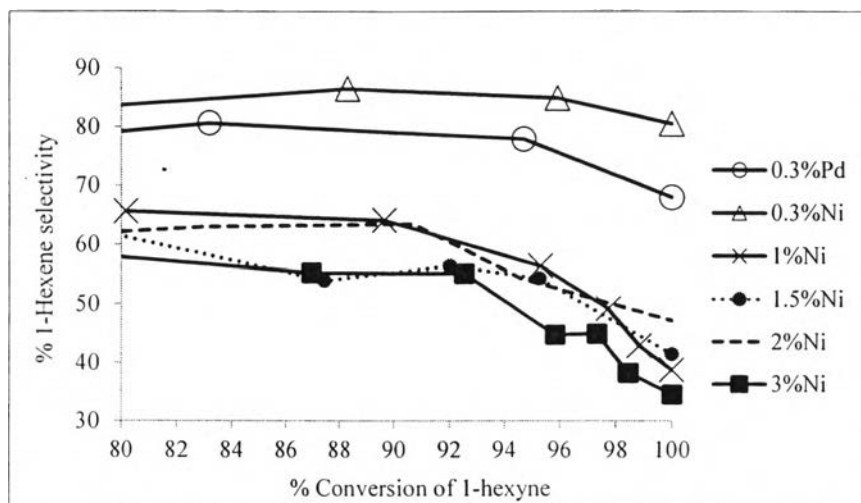
**Figure 4.2** 1-Hexene selectivity (%) as a function of time for Pd/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.

The yield of 1-hexene as a function of reaction time is shown in Fig. 4.3. The results illustrate that 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> exhibits the highest 1-hexene yield. As observed, 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> shows similar 1-hexene yield as 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at 2 hours. However, 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> exhibits the depletion of 1-hexene yield after 2 hours possibly the subsequent hydrogenation of 1-hexene to *n*-hexane. Obviously, 1-hexene yield decreases dramatically when 1%Ni/Al<sub>2</sub>O<sub>3</sub>, 1.5%Ni/Al<sub>2</sub>O<sub>3</sub>, 2%Ni/Al<sub>2</sub>O<sub>3</sub>, and 3%Ni/Al<sub>2</sub>O<sub>3</sub> is used. The high activity of Ni/Al<sub>2</sub>O<sub>3</sub> at Ni loading 1%Ni, 1.5%Ni, 2%Ni, and 3%Ni to further hydrogenate 1-hexene to *n*-hexane causes the reduction of 1-hexene yield.

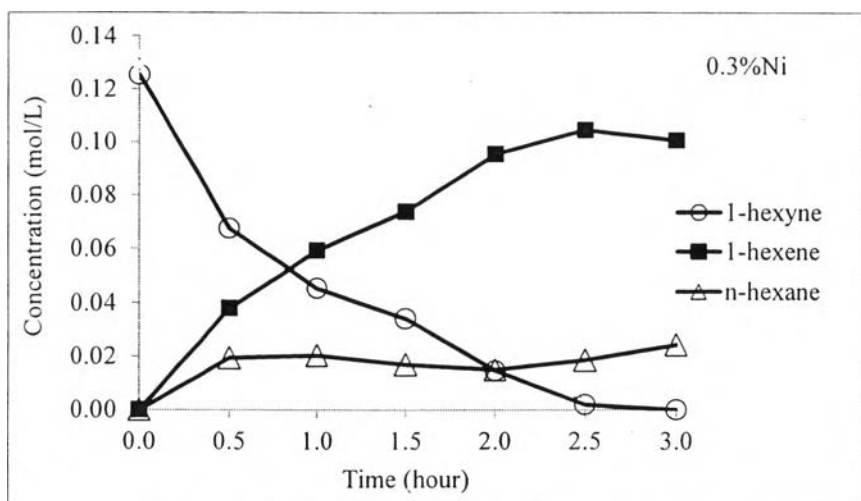


**Figure 4.3** 1-Hexene yield (%) as a function of time for Pd/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.

The relation of 1-hexene selectivity and 1-hexyne conversion for Pd and Ni on alumina catalysts is shown in Fig. 4.4. As expected, 1-hexene selectivity decreases significantly with increasing 1-hexyne conversion due to subsequent hydrogenation of 1-hexene to *n*-hexane. The 0.3wt% of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the highest 1-hexene selectivity, while 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> shows lower 1-hexene selectivity than 0.3%Ni/Al<sub>2</sub>O<sub>3</sub>. The 1-hexene selectivity of the catalysts is decreasing in the order: 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> > 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> > 2%Ni/Al<sub>2</sub>O<sub>3</sub> > 1.5%Ni/Al<sub>2</sub>O<sub>3</sub> > 1%Ni/Al<sub>2</sub>O<sub>3</sub> > 3%Ni/Al<sub>2</sub>O<sub>3</sub> at completed conversion. Furthermore, the changes of 1-hexyne, 1-hexene and *n*-hexane concentration with reaction time when using 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 4.5. It can be observed that, 1-hexyne decreases with the reaction time, while the 1-hexene is significantly increased with reaction time, and *n*-hexane is relatively constant indicating that the subsequent hydrogenation of 1-hexene is not important due to retard reaction. However, after the conversion of 1-hexyne is completed, 1-hexene is then hydrogenated to *n*-hexane.



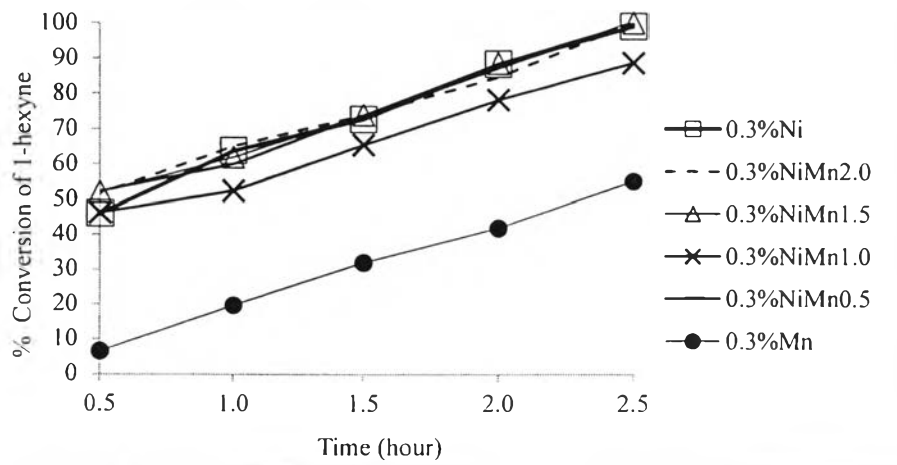
**Figure 4.4** 1-Hexene selectivity (%) as a function of conversion (%) for Pd/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.



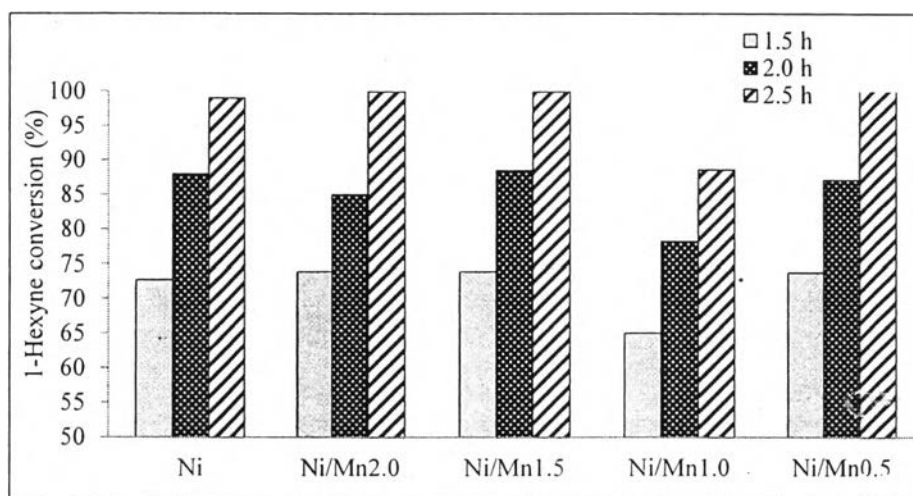
**Figure 4.5** Concentration of reactant and products as a function of reaction time for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> monometallic catalysts.

#### 4.1.2 Ni-Mn Bimetallic Supported on Alumina Catalyst

The activity of 1-hexyne hydrogenation by Mn-Ni/Al<sub>2</sub>O<sub>3</sub> with various Ni/Mn molar ratios is showed in Fig. 4.6 and Fig. 4.7. The results illustrate that the activity of 1-hexyne hydrogenation increases linearly with the reaction time. It is found that Ni/Al<sub>2</sub>O<sub>3</sub>, NiMn2.0/Al<sub>2</sub>O<sub>3</sub>, NiMn1.5/Al<sub>2</sub>O<sub>3</sub>, and NiMn0.5/Al<sub>2</sub>O<sub>3</sub> show high activity, while NiMn1.0/Al<sub>2</sub>O<sub>3</sub> exhibits the lowest activity among Ni-Mn bimetallic catalysts. For Mn/Al<sub>2</sub>O<sub>3</sub> shows relatively low activity.



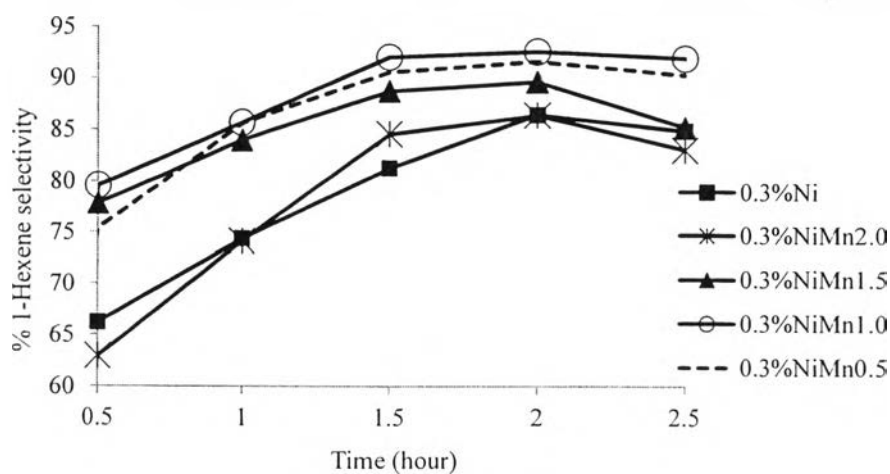
**Figure 4.6** 1-Hexyne total conversions (%) as a function of time for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.



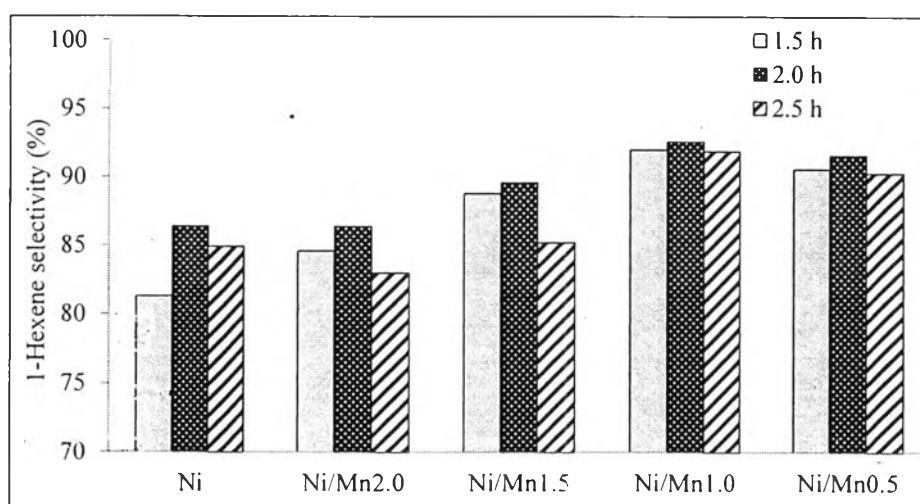
**Figure 4.7** 1-Hexyne total conversions (%) at 1.5 h., 2.0 h., and 2.5 h. for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.

Fig. 4.8 and Fig. 4.9 illustrate 1-hexene selectivity as a function of reaction time for Ni-Mn on alumina catalysts. The catalysts exhibit the increase of 1-hexene selectivity with reaction time. However, the catalysts show the decrease of 1-hexene selectivity after 2.0 hours due to the activity toward 1-hexene hydrogenation to *n*-hexane. NiMn1.0/Al<sub>2</sub>O<sub>3</sub> exhibits the highest 1-hexene selectivity, while Ni/Al<sub>2</sub>O<sub>3</sub> and NiMn2.0/Al<sub>2</sub>O<sub>3</sub> show relatively low 1-hexene selectivity. The

1-hexene selectivity exhibits in the order: NiMn1.0 > NiMn0.5 > NiMn1.5 > NiMn2.0 ≈ Ni.



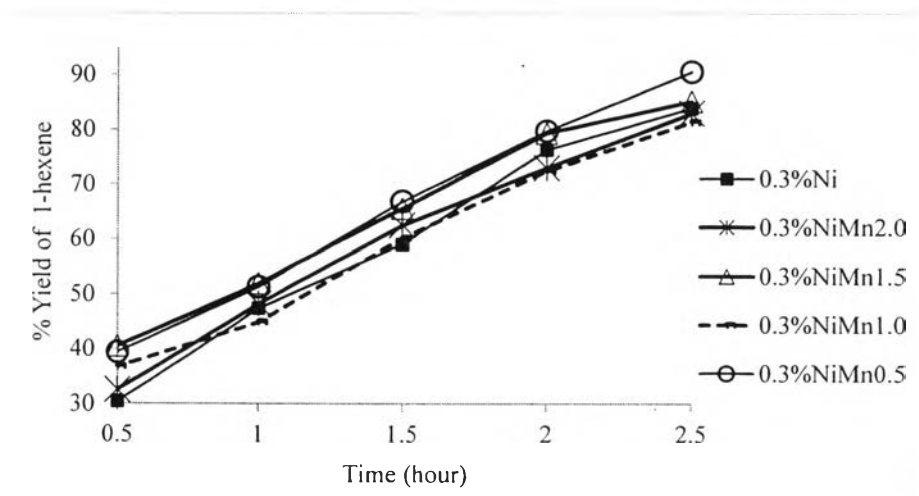
**Figure 4.8** 1-Hexene selectivity (%) as a function of time for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.



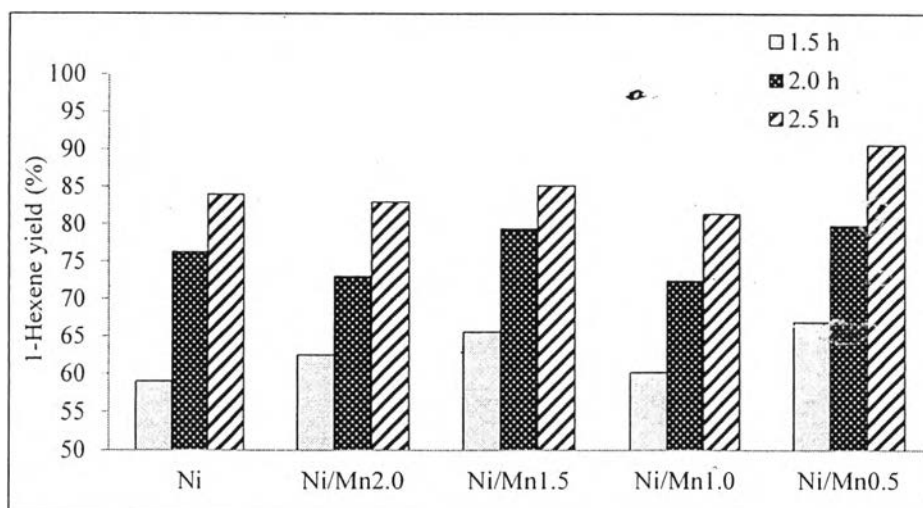
**Figure 4.9** 1-Hexene selectivity (%) at 1.5 h., 2.0 h., and 2.5 h. for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.

The yield of 1-hexene as a function of reaction time is shown in Fig. 4.10 and Fig. 4.11. The catalysts show the increase of 1-hexene yield with the

reaction time. The results illustrate that both NiMn1.5/Al<sub>2</sub>O<sub>3</sub> and NiMn0.5/Al<sub>2</sub>O<sub>3</sub> exhibit higher 1-hexene yield than Ni/Al<sub>2</sub>O<sub>3</sub>, while NiMn1.0/Al<sub>2</sub>O<sub>3</sub> provides relatively low 1-hexene yield due to low activity. The NiMn0.5/Al<sub>2</sub>O<sub>3</sub> provides the highest 1-hexene yield 91% at completed conversion.

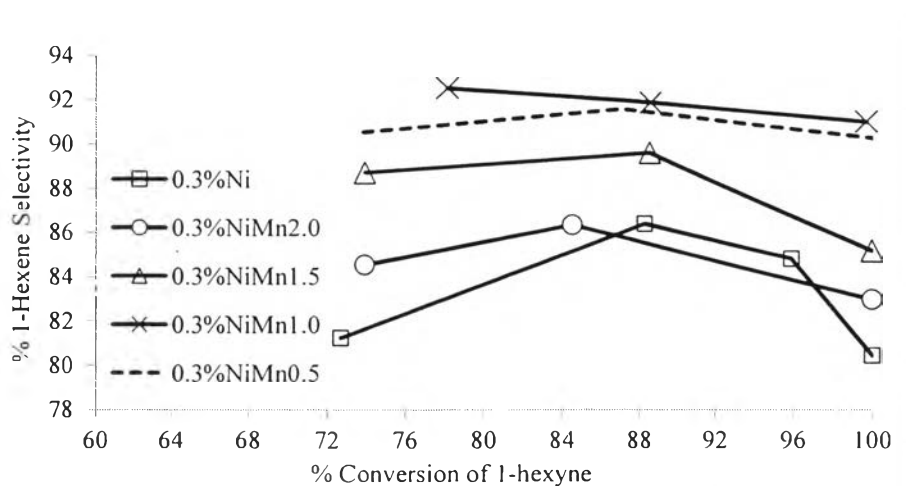


**Figure 4.10** 1-Hexyne yield (%) as a function of time for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.



**Figure 4.11** 1-Hexene yield (%) at 1.5h, 2.0h, and 2.5h. for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.

The relation of 1-hexene selectivity and 1-hexyne conversion for Ni-Mn at various molar ratios on alumina catalysts is shown in Fig. 4.12. As observed, 1-hexene selectivity decreases significantly at nearly completed conversion due to subsequent hydrogenation of 1-hexene to *n*-hexane. The NiMn1.0/Al<sub>2</sub>O<sub>3</sub> exhibits the highest 1-hexene selectivity, while Ni/Al<sub>2</sub>O<sub>3</sub> and NiMn2.0/Al<sub>2</sub>O<sub>3</sub> show relatively low. These results show that the 1-hexene selectivity of the catalysts is decreasing in the order: NiMn1.0 > NiMn0.5 > NiMn1.5 > NiMn2.0 > Ni at completed conversion.

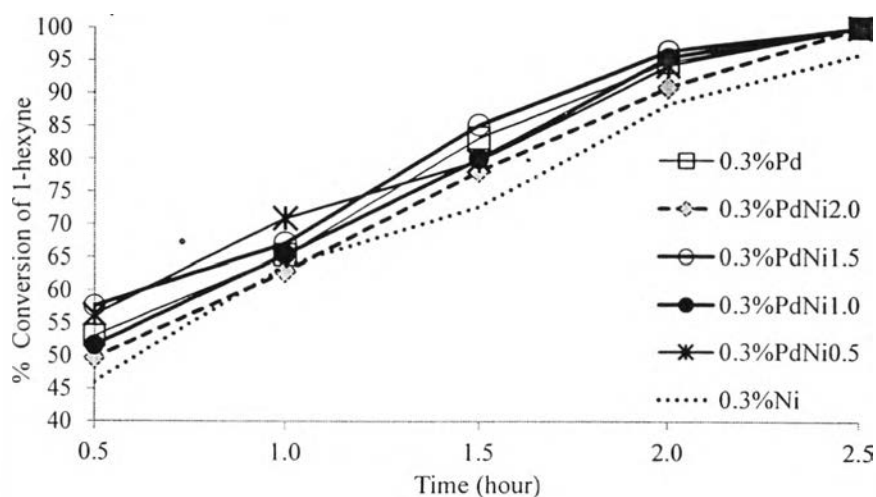


**Figure 4.12** 1-Hexene selectivity (%) as a function of conversion (%) for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> at various Ni/Mn ratios.

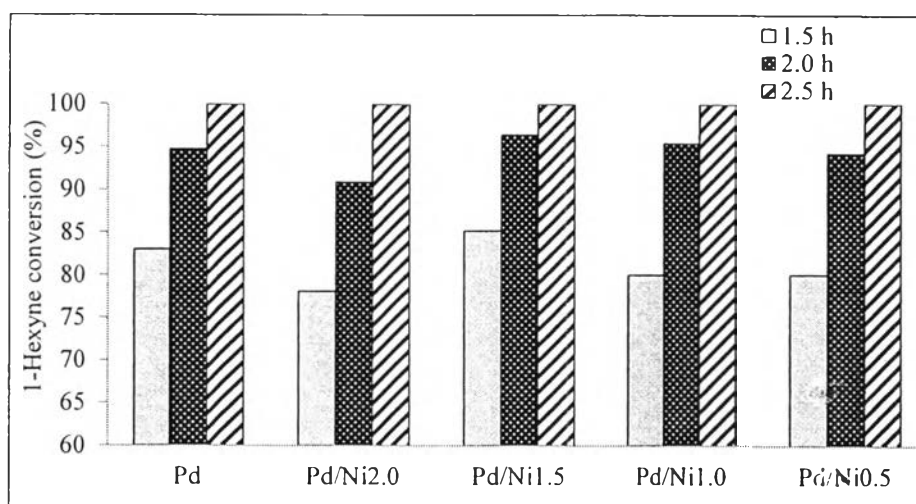
#### 4.1.3 Pd-Ni Bimetallic Supported on Alumina Catalyst

The activity of 1-hexyne hydrogenation by Ni-Pd/Al<sub>2</sub>O<sub>3</sub> with various Pd/Ni molar ratios is shown in Fig. 4.13 and Fig. 4.14. The results illustrate that the activity of 1-hexyne hydrogenation increases with the reaction time. As observed at 1.5 and 2.0 hours, PdNi1.5/Al<sub>2</sub>O<sub>3</sub> shows higher activity than Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, while PdNi2.0/Al<sub>2</sub>O<sub>3</sub> exhibits the lowest in the activity among Pd-Ni bimetallic catalysts. However, all the Pd-Ni bimetallic catalysts access to 100% conversion within 2.5 hours. For Ni/Al<sub>2</sub>O<sub>3</sub> exhibits relatively low activity.





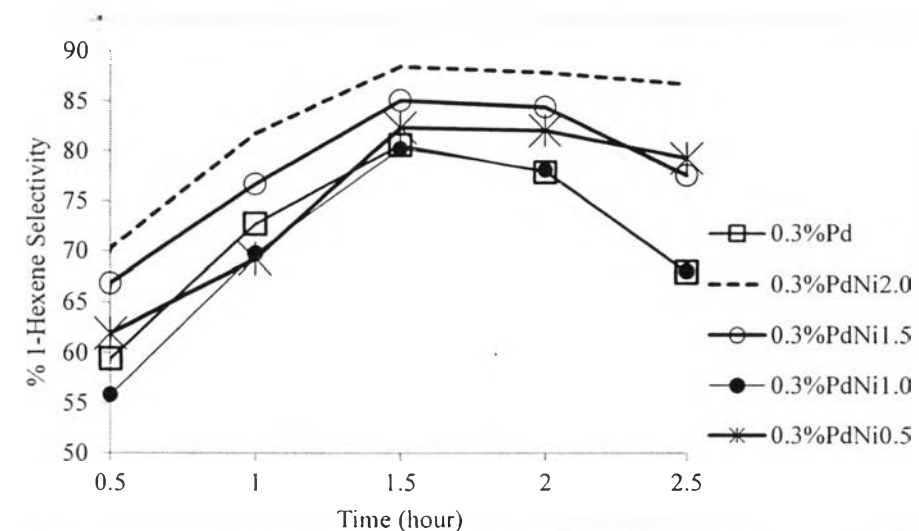
**Figure 4.13** 1-Hexyne total conversions (%) as a function of time for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.



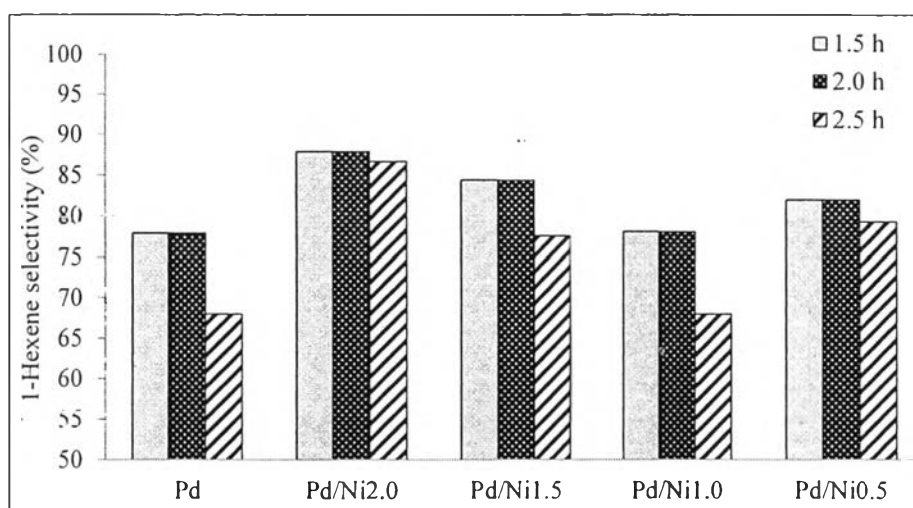
**Figure 4.14** 1-Hexyne total conversions (%) at 1.5h, 2.0h, and 2.5h for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.

Fig. 4.15 and Fig. 4.16 illustrate 1-hexene selectivity as a function of reaction time for Pd-Ni on alumina catalysts. The catalysts exhibit the increase of 1-hexene selectivity with reaction time. After 1.5 hours, the catalysts show the decrease of 1-hexene selectivity with reaction time probably the activity toward 1-hexene hydrogenation to *n*-hexane. PdNi2.0/Al<sub>2</sub>O<sub>3</sub> exhibits the highest 1-hexene

selectivity, while Pd/Al<sub>2</sub>O<sub>3</sub> shows relatively low 1-hexene selectivity. The 1-hexene selectivity is exhibited in the order: PdNi2.0 > PdNi1.5 > PdNi0.5 > PdNi1.0 ≈ Pd.



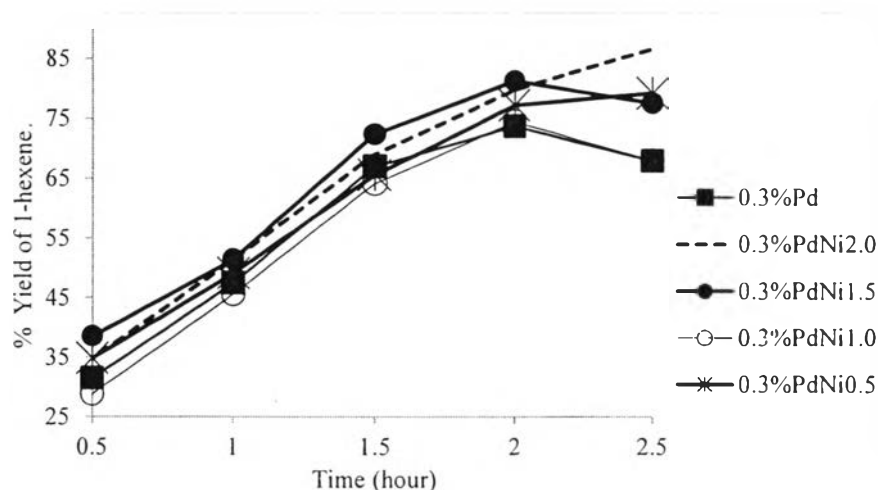
**Figure 4.15** 1-Hexene selectivity (%) as a function of time for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.



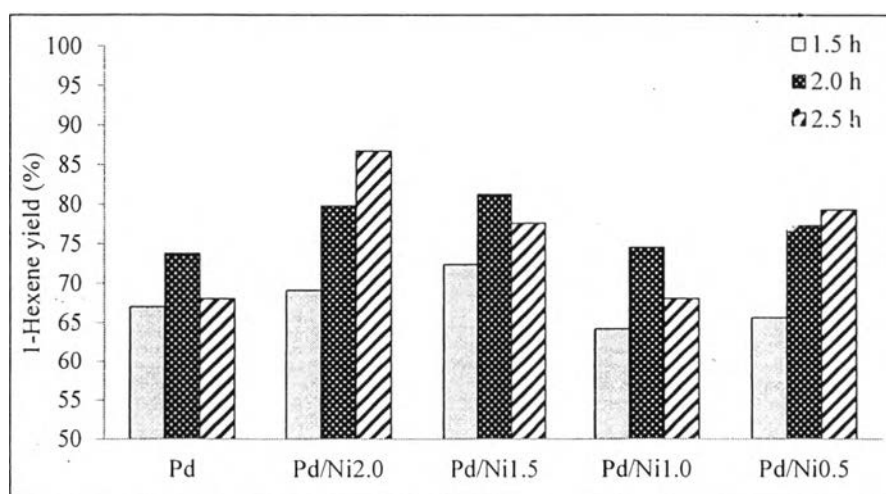
**Figure 4.16** 1-Hexene selectivity (%) at 1.5 h., 2.0 h., and 2.5 h. for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.

The yield of 1-hexene as a function of reaction time is shown in Fig. 4.17. The catalysts show the increase of 1-hexene yield with reaction time,

PdNi2.0/Al<sub>2</sub>O<sub>3</sub> and PdNi1.5/Al<sub>2</sub>O<sub>3</sub> exhibit higher 1-hexene yield than Pd/Al<sub>2</sub>O<sub>3</sub>, while PdNi1.0/Al<sub>2</sub>O<sub>3</sub> shows low 1-hexene yield due to low 1-hexene selectivity. After 2.0 hours, the catalysts exhibit the decrease of 1-hexene yield with reaction time due to the activity of 1-hexene to *n*-hexane. Except PdNi2.0/Al<sub>2</sub>O<sub>3</sub>, this is indicated that the subsequent hydrogenation of 1-hexene probably not important due to relatively low activity.

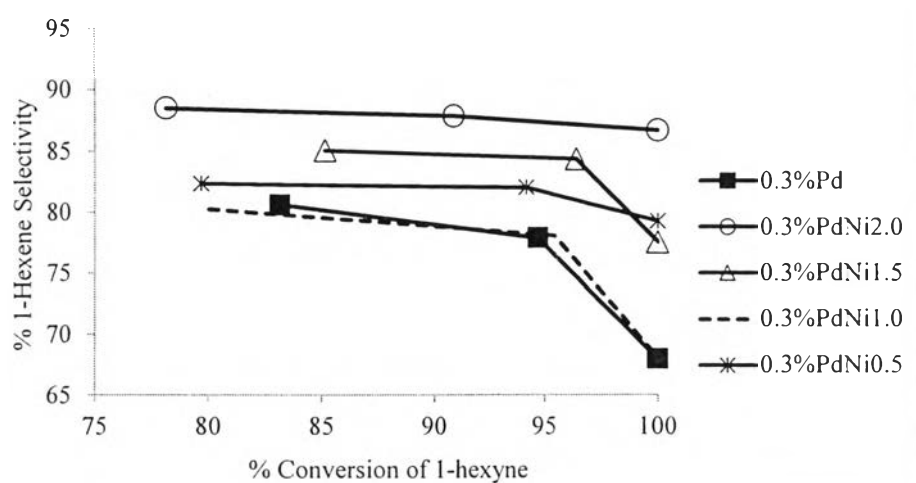


**Figure 4.17** 1-Hexyne yield (%) as a function of time for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.



**Figure 4.18** 1-Hexyne yield (%) at 1.5 h., 2.0 h., and 2.5 h. for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios.

The relation of 1-hexene selectivity and 1-hexyne conversion for Pd-Ni on alumina catalysts is shown in Fig. 4.19. As expected, 1-hexene selectivity decreases significantly at nearly completed conversion due to the hydrogenation of 1-hexene to *n*-hexane. The 0.3%PdNi2.0 exhibits the highest 1-hexene selectivity, which is decreased slightly at completed conversion. These results show that the 1-hexene selectivity of the catalysts is decreasing in the order: 0.3%PdNi2.0 > 0.3%PdNi1.5 > 0.3%PdNi0.5 > 0.3%PdNi1.0  $\approx$  0.3%Pd.



**Figure 4.19** 1-Hexene selectivity (%) as a function of conversion (%) for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> at various Pd/Ni ratios

## 4.2 Catalytic Characterization

### 4.2.1 Catalyst Characterization by BET and H<sub>2</sub>-chemisorption

#### 4.2.1.1 *Pd and Ni Supported on Alumina Catalysts*

The surface area, pore volume, and pore size of Pd and Ni monometallic catalysts are shown in Table 4.1. The catalysts surface area is decreased with increasing metal loading. This implies that the metal particles possibly block the pores of alumina causing the reduction of surface area and pore volume. The average pore diameter of the catalysts are around 12-18 nm, while supported alumina has average pore diameter of 20 nm. For the H<sub>2</sub>-chemisorption, the results in term of mole of chemisorbed hydrogen per total metal mole are shown in Table 4.1. At the same level of metal loading, 0.3% Pd exhibits higher H<sub>2</sub> adsorption than 0.3%Ni. Furthermore, it can be observed that the H<sub>2</sub> adsorption increases with increasing Ni loading (1% Ni > 0.3% Ni). This implies that at low loaded metal, the agglomeration of metal probably not important. At higher Ni loading (higher than 1%), the H<sub>2</sub> chemisorption is reduced indicating lowering Ni dispersion on alumina surface, as a result, the rate of hydrogenation is decreased as indicated in Figure 4.1.

**Table 4.1** The catalysts surface area, pore volume, average pore diameter, and hydrogen chemisorption of Pd/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

Catalysts	Analytical mode			
	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average Pore diameter (nm)	H <sub>2</sub> adsorbed (H/metal)
Al <sub>2</sub> O <sub>3</sub>	99	0.55	20	N/A
0.3%Pd/A	73	0.36	18	0.40
0.3%Ni/A	76	0.38	14	0.24
1%Ni/A	38	0.35	16	0.34
1.5%Ni/A	37	0.31	14	0.28
2%Ni/A	32	0.33	15	0.21
3%Ni/A	26	0.32	12	0.20

#### 4.2.1.2 Ni-Mn Supported on Alumina Catalysts

The surface area, pore volume, and pore diameter of Ni-Mn bimetallic catalysts at various Ni/Mn molar ratios are shown in Table 4.2. The catalysts surface area is decreased with increasing Mn loading. The average pore diameter of the Ni-Mn catalysts are around 7.1-8.1 nm, while Ni/Al<sub>2</sub>O<sub>3</sub> has average pore diameter of 14 nm. For the H<sub>2</sub>-chemisorption, the results in term of molar ratio of chemisorbed hydrogen per total mole of Ni (H<sub>2</sub>/Ni) are shown in Table 4.2. It can be observed that increase amount of Mn exhibits the H<sub>2</sub>/Ni ratio decreased significantly. Interestingly, Ni/Mn ratio 0.5 exhibits higher H<sub>2</sub> adsorption than Ni/Mn ratio 1.0, this implies that loading of Mn at Ni/Mn ratio 0.5 shows the dispersion of catalyst higher than ratio 1.0 resulting higher activity.

**Table 4.2** The catalysts surface area, pore volume, average pore diameter, and hydrogen chemisorption of Ni-Mn catalysts

Catalysts	Analytical mode			
	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average Pore diameter (nm)	H <sub>2</sub> adsorbed (H <sub>2</sub> /Ni)
Al <sub>2</sub> O <sub>3</sub>	99	0.55	20	N/A
0.3%Mn/Al <sub>2</sub> O <sub>3</sub>	67	0.31	9.6	N/A
0.3%Ni/Al <sub>2</sub> O <sub>3</sub>	76	0.38	14	0.24
0.3%NiMn2.0/Al <sub>2</sub> O <sub>3</sub>	68	0.22	8.1	0.22
0.3%NiMn1.5/Al <sub>2</sub> O <sub>3</sub>	65	0.26	8.0	0.20
0.3%NiMn1.0/Al <sub>2</sub> O <sub>3</sub>	63	0.30	7.5	0.13
0.3%NiMn0.5/Al <sub>2</sub> O <sub>3</sub>	61	0.28	7.1	0.18

#### 4.2.1.3 Pd-Ni Supported on Alumina Catalysts

The surface area, pore volume, and pore diameter of Pd-Ni bimetallic catalysts at various Pd/Ni molar ratios are shown in Table 4.3. The catalysts surface area is decreased with increasing Ni loading. The average pore diameter of Pd-Ni catalysts are around 11-16 nm, while Pd/Al<sub>2</sub>O<sub>3</sub> has average pore diameter of 18 nm. For the H<sub>2</sub>-chemisorption, the results in term of mole of chemisorbed hydrogen per total mole of Pd are shown in Table 4.3. It can be observed that adding of Ni on Pd-based catalyst shows the reduction of H<sub>2</sub> adsorption

probably part of Pd on the surface cluster is covered by Ni. Pd/Ni at ratio 1.5 shows higher H<sub>2</sub> adsorption than other prepared Ni-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, this is implied that loading of Ni at Pd/Ni ratio 1.5 provides higher dispersion of catalyst than other Pd-Ni catalysts resulting high activity.

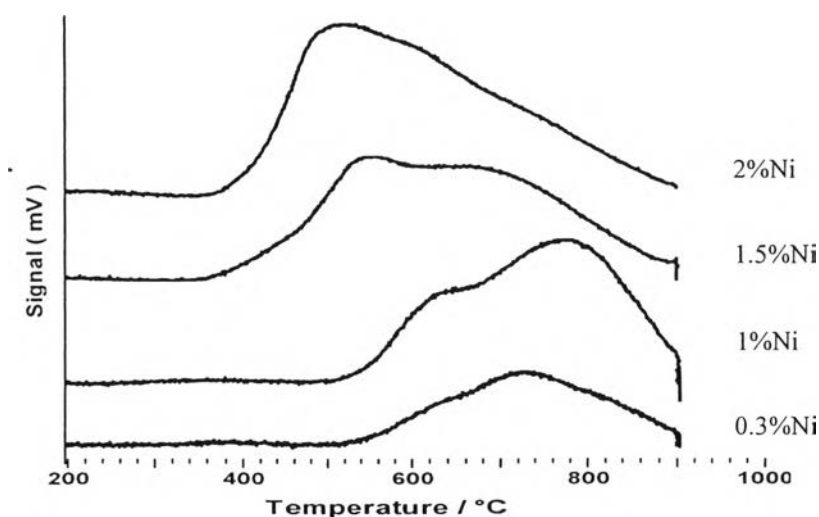
**Table 4.3** The catalysts surface area, pore volume, average pore diameter, and hydrogen chemisorption of Pd-Ni catalysts

Catalysts	Analytical mode			
	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average Pore diameter (nm)	H <sub>2</sub> adsorbed (H <sub>2</sub> /Pd)
Al <sub>2</sub> O <sub>3</sub>	99	0.55	20	N/A
0.3%Ni/Al <sub>2</sub> O <sub>3</sub>	76	0.38	14	0.24
0.3%Pd/Al <sub>2</sub> O <sub>3</sub>	78	0.40	18	0.40
0.3%PdNi2.0/Al <sub>2</sub> O <sub>3</sub>	68	0.24	14	0.20
0.3%PdNi1.5/Al <sub>2</sub> O <sub>3</sub>	73	0.38	16	0.38
0.3%PdNi1.0/Al <sub>2</sub> O <sub>3</sub>	68	0.31	11	0.27
0.3%PdNi0.5/Al <sub>2</sub> O <sub>3</sub>	75	0.35	12	0.24

#### 4.2.2 Temperature Program Reduction (TPR)

##### 4.2.2.1 *Ni Supported on Alumina Catalysts*

TPR profiles for 0.3%Ni/Al<sub>2</sub>O<sub>3</sub>, 1%Ni/Al<sub>2</sub>O<sub>3</sub>, 1.5%Ni/Al<sub>2</sub>O<sub>3</sub>, and 2%Ni/Al<sub>2</sub>O<sub>3</sub> supported on alumina catalysts are illustrated in Fig. 4.20. The TPR peak of 0.3%Ni/Al<sub>2</sub>O<sub>3</sub> observed at 740 °C attributed to NiO species which indicates strong interaction with support. As amount of Ni loading increases, the reduction temperature of NiO species shifts to lower temperature possibly because the less interaction of NiO and alumina surface due to metal agglomeration. At high nickel loading, the alumina is saturated with Ni and bulk NiO is formed on the alumina surface (Li *et al.*, 1995). As expected, the H<sub>2</sub> adsorption and catalyst activity decrease when 1.5%Ni/Al<sub>2</sub>O<sub>3</sub>, 2%Ni/Al<sub>2</sub>O<sub>3</sub>, and 3%Ni/Al<sub>2</sub>O<sub>3</sub> are used.

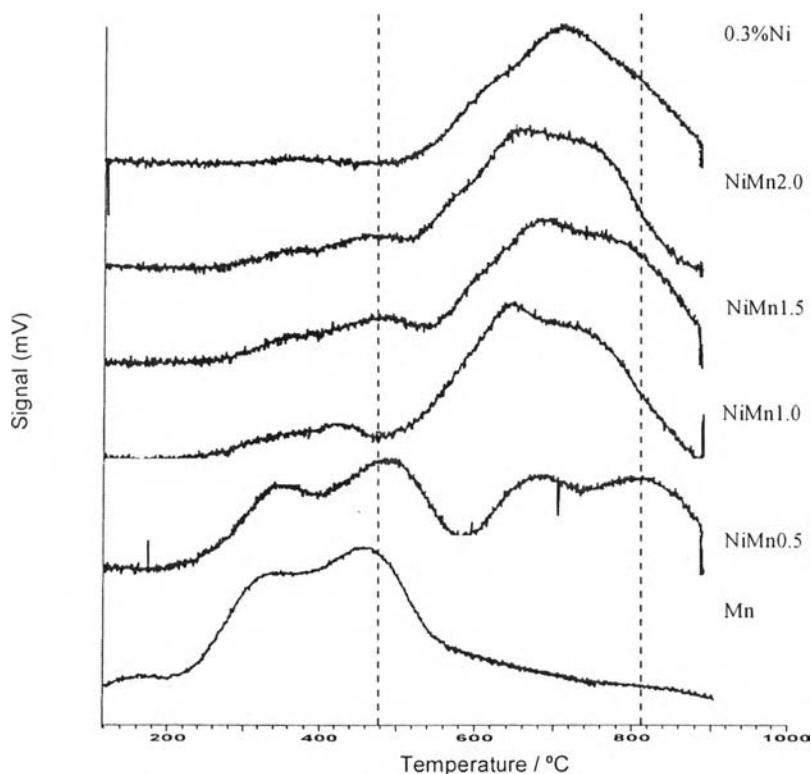


**Figure 4.20** Temperature programmed reduction (TPR) profile of Ni supported on alumina catalysts.

#### 4.2.2.2 Ni-Mn Supported on Alumina Catalysts

Fig. 4.21 exhibits the TPR profile for Ni-Mn with various Ni/Mn molar ratios supported on alumina catalysts. The increase amount of Mn on Ni/Al<sub>2</sub>O<sub>3</sub> can be observed the increase of H<sub>2</sub> consumption peak of manganese oxide species at 360 °C and 500 °C. Kim *et al.* (2010) suggested that the reduction of the first reduction peak is caused by the reduction of MnO<sub>2</sub> (Mn<sup>+4</sup>) to Mn<sub>2</sub>O<sub>3</sub> (Mn<sup>+3</sup>) and the other reduction peak is attributed to the reductions of Mn<sub>2</sub>O<sub>3</sub> (Mn<sup>+3</sup>) to MnO (Mn<sup>+2</sup>) via Mn<sub>3</sub>O<sub>4</sub>. Interestingly, Ni/Mn ratio 1.0 shows the reduction of MnO shifts to lower temperature probably, which suggests that Mn particles agglomerate instead isolate on the support indicating weak interaction with support. This result agrees with the lowest hydrogenation activity when NiMn1.0/Al<sub>2</sub>O<sub>3</sub> is used. The TPR peak at 820 °C is more obvious when the amount of Mn is increased on Ni-based catalyst. Malaibari *et al.* (2015) reported that the increase in the reduction temperature of impregnated catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>) was attributed to the interaction of NiO-Al<sub>2</sub>O<sub>3</sub>-MoO<sub>x</sub>.



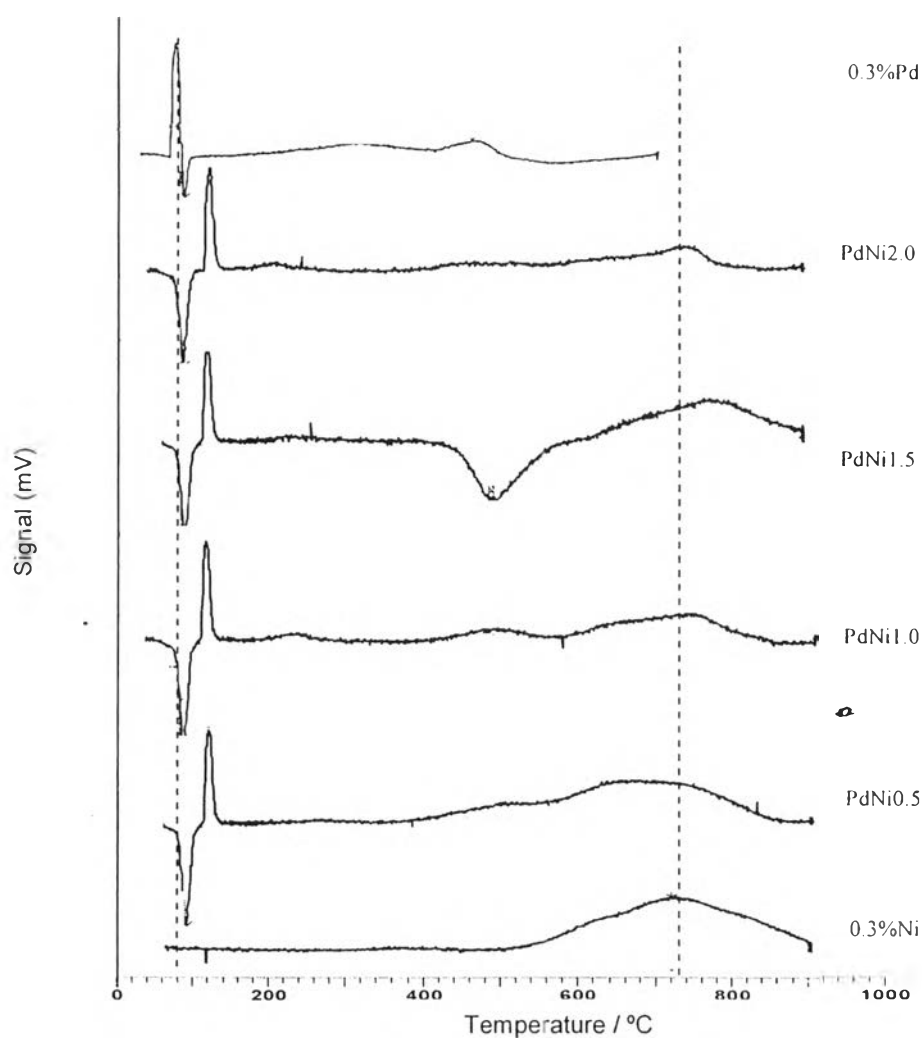


**Figure 4.21** Temperature programmed reduction (TPR) profile of Ni-Mn supported on alumina catalysts.

#### 4.2.2.3 Pd-Ni Supported on Alumina Catalysts

TPR profile for Pd-Ni supported on alumina catalysts are shown in Figure 4.22. The results illustrate that the Pd monometallic and Pd-Ni bimetallic catalysts can be observed a single negative peak at 90 °C attributed to desorption of hydrogen from the decomposition of  $\beta$ -Pd hydride (Navarro *et al.*, 2000). According to Ferrer *et al.* (2005), the formation of PdH<sub>x</sub> phases is favored by the existence of large palladium particles. TPR profile of Pd/Al<sub>2</sub>O<sub>3</sub> shows the H<sub>2</sub>-consumption peak at around 80 °C which is the reduction of PdO crystallites to metallic Pd. Adding amount of Ni to Pd-based catalyst causes the reduction peak of PdO in TPR to shifts 40 °C higher. The shift of PdO TPR peak to higher temperature suggests the harder for reduction of PdO to metallic Pd. It is well known that the strong interaction between palladium oxide and promoted metal probably significant

increases the reduction temperature of Pd precursors (Pellegrini *et al.*, 2009). The reduction of PdO and the desorbed hydrogen of  $\beta$ -Pd hydride are also agreed with the work done by Wang *et al.* (2002). Considering the reduction peak of nickel oxide at around 730 °C, Pd/Ni at ratio 1.5 exhibits the reduction peak of nickel oxide shifts to higher temperature attributed to portion of excess nickel are isolated on support causing high metal dispersion and exhibits strong interaction with support.



**Figure 4.22** Temperature programmed reduction (TPR) profile of Pd-Ni supported on alumina catalysts.