

## CHAPTER IV

### RESULTS AND DISCUSSION

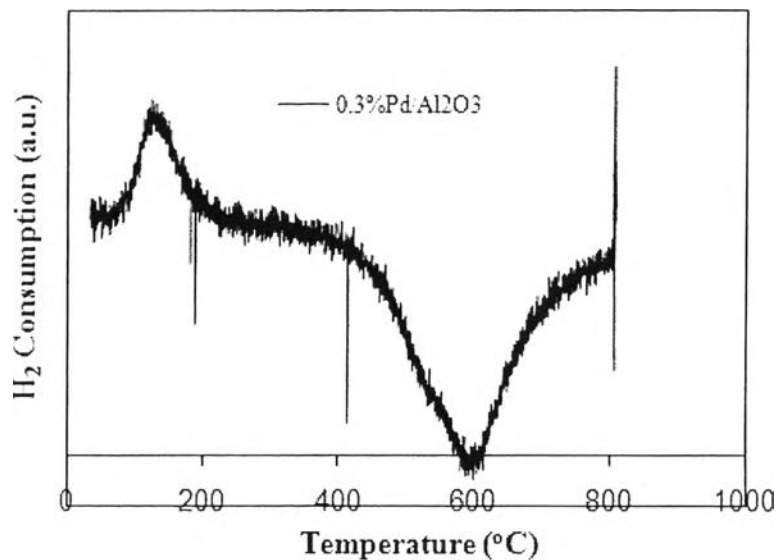
#### 4.1 Catalytic Characterization

##### 4.1.1 Temperature Program Reduction (TPR)

This method is used to examine the reducibility of palladium, Copper and Tungsten species on the alumina support.

##### *4.1.1.1 Low loaded Pd Supported on Alumina Catalyst*

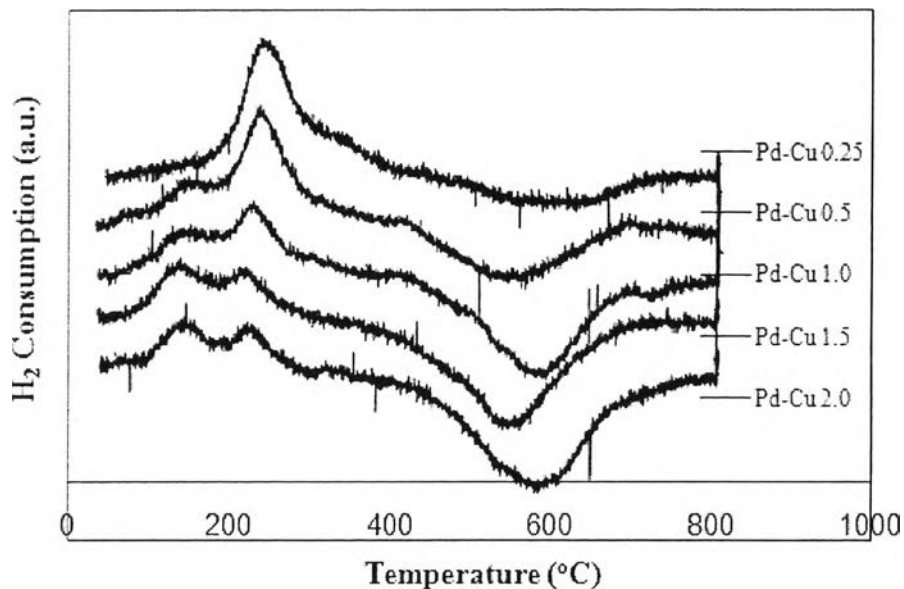
TPR profile for 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is shown in Figure 4.1. Panpranot *et al.*(2004) reported that Pd on catalytic support prepared from using palladium nitrate was in the form of PdO species agglomerated on the support surface. If PdO species interact weakly with the supports, the PdO species can be reduced readily to be H<sub>x</sub>Pd (Palladium hydride) at an ambient temperature when hydrogen is introduced into the system (not shown in Fig 4.1), as demonstrated by Panpranot *et al.*(2004). The palladium hydride would generate H<sub>2</sub> when raising the temperature to around 600 °C, as an inverse peak. From Figure 4.1, it can be seen that there had two peaks, a main hydrogen consumption peak at around 140-150 °C which can be attributed to the reduction of PdO species on the support surface and a significant negative peak at around 560-600 °C was observed for all the catalysts; this peak can be attributed to the decomposition of β-Pd hydride (Lieske *et al.*, 1985). In addition, there had not a peak of H<sub>x</sub>Pd (Palladium hydride) at an ambient temperature. Therefore, it could be concluded that PdO species on the 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst interact strongly with the supports. It has previously been reported that there was a strong metal support interaction between metal and alumina support.



**Figure 4.1:** TPR profile of 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### 4.1.1.2 Pd-Cu Supported on Alumina Catalysts

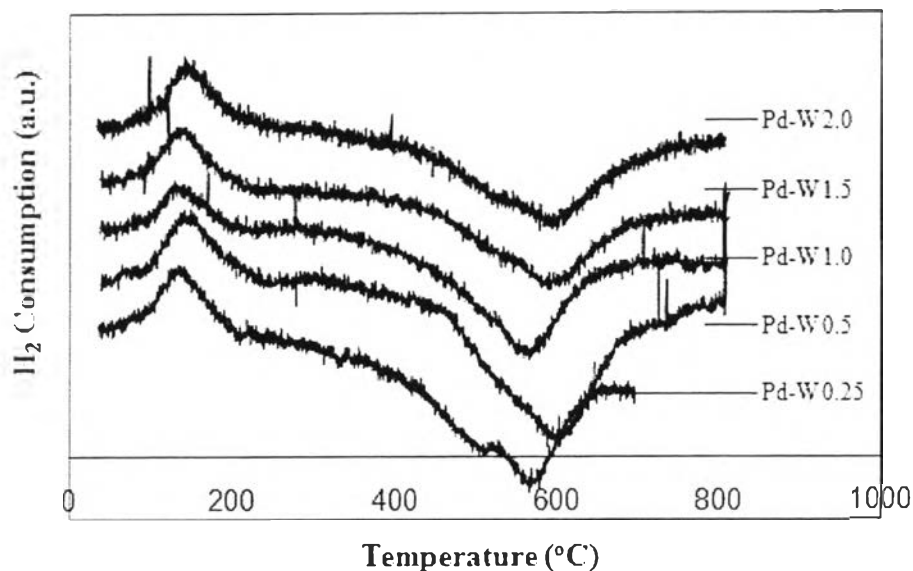
TPR profiles of Pd-Cu/Al<sub>2</sub>O<sub>3</sub> with various Pd/Cu atomic ratios are shown in Figure 4.2. They are composed of three peaks. The positive peak at around 110-160 °C can be attributed to the reduction of (Cu and Pd), (Cu or Pd) in mixed oxide (PdxCuyO), a positive peak at around 220-300 °C are the reduction peak of CuO which has no interaction with Pd (Batista et al., 2001) and a significant negative peak at around 560-600 °C can be attributed to the decomposition of  $\beta$ -Pd hydride (Lieske *et al.*, 1985). From the TPR profiles, it indicated that all of Pd-Cu catalysts composed of three components which Pd, Cu which had interaction with Pd and had no interaction with Pd. When focusing on all negative peaks at around 560-600 °C, it can be concluded that more PdO species as for Pd to Cu ratio of 2, the more H<sub>2</sub> generated. Lopez-Gaona *et al.* (2010) suggested that such an inverse peak effect might be indicative of large Pd particles on the supports. The peak became more negative when Pd concentration on the supports increased, resulting in the higher release of chemisorbed hydrogen. Moreover, the amount of H<sub>2</sub> released from Pd could decrease when the metal dispersion increased. It also found that increasing the Cu species, the reduction of (Cu and Pd), (Cu or Pd) in mixed oxide (PdxCuyO) decreases possibly due to Cu species likely interact to each other more than interact with Pd species to form mixed oxide (PdxCuyO).



**Figure 4.2:** TPR profiles of 0.3% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts at various Cu loadings.

#### 4.1.1.3 Pd-W Supported on Alumina Catalysts

TPR profiles of Pd-W/Al<sub>2</sub>O<sub>3</sub> with various Pd/W atomic ratios are shown in Figure 4.3. It can be seen that there have a reduction pattern very similar to the 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> one. A main hydrogen consumption peak at around 140-150 °C can be attributed to the reduction of PdO species on the support surface and a negative peak at around 560-600 °C can be attributed to the decomposition of β-Pd hydride (Lieske *et al.*, 1985). Furthermore, it also found that, there had no the reduction peak of amorphous oxidized W species because it would take place at high temperature (>950 °C) (Lederhos *et al.*, 2011) and Busto *et al.* (2008) also suggested that during reduction of tungsten oxides in hydrogen stream, there have four reduction stages occur including (i) in range of 300 °C -500 °C, WO<sub>3</sub> would be converted to substoichiometric WO<sub>2.9</sub>, (ii) the WO<sub>2.9</sub> compound would be converted into WO<sub>2</sub> in range of 550 °C -700 °C, (iii) the reduction of WO<sub>2</sub> to W<sup>0</sup> would occur in the 750 °C -850 °C, and (iv) at high temperature (>900 °C), the reduction of WO<sub>x</sub> species with strong interaction with support would occur.



**Figure 4.3:** TPR profiles of 0.3% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts at various W loadings.

#### 4.1.2 H<sub>2</sub> Chemisorption

H<sub>2</sub> chemisorption results were expressed in terms of the ratio between mole of chemisorbed H<sub>2</sub> and total mole of added Pd (H/Pd) which correspond to the amount of Pd on the surface of metal cluster of the catalysts because H<sub>2</sub> chemisorption can only occur on Pd under investigated condition. (Furlong *et al.*, 1994), (Lederhos, C.R. *et al.*, 2011)

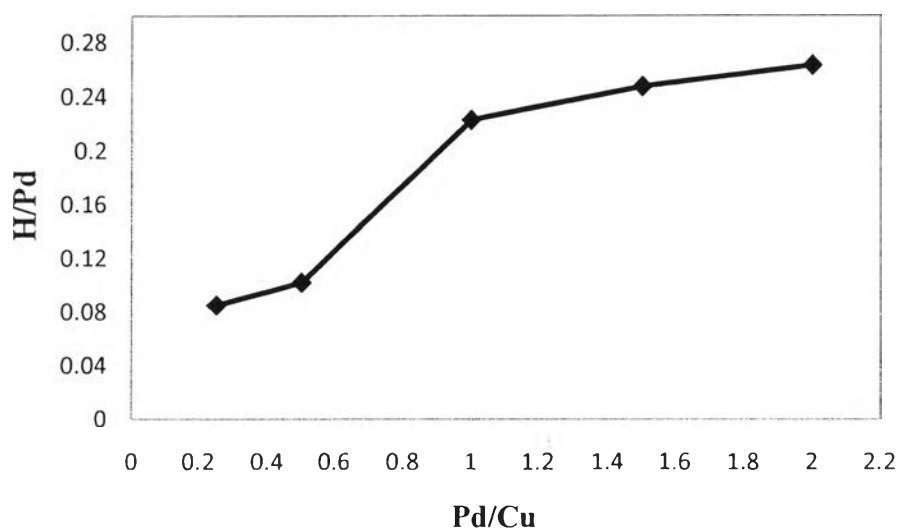
##### 4.1.2.1 *Low loaded Pd Supported on Alumina Catalyst*

The H<sub>2</sub> chemisorption result of 0.3%Pd catalyst is equal to 0.572. From the results showed that 0.3%Pd catalyst gave the highest H/Pd ratio when it was compared with Pd-Cu/Al<sub>2</sub>O<sub>3</sub> in Figure 4.4. It indicated that 0.3%Pd catalyst exhibited the highest amount of Pd at surface.

##### 4.1.2.2 *Pd-Cu Supported on Alumina Catalysts*

The H<sub>2</sub> chemisorption results of Pd-Cu supported on alumina catalysts with various Pd/Cu ratios are shown in Figure 4.4. When adding low amount of Cu, the H/Pd ratio slightly changed possibly due to Pd at the surface of metal cluster was not much diluted by the added Cu. At the amount of Cu higher than 0.18 wt%, the H/Pd ratio dramatically decreases. It suggests that Pd at the surface of

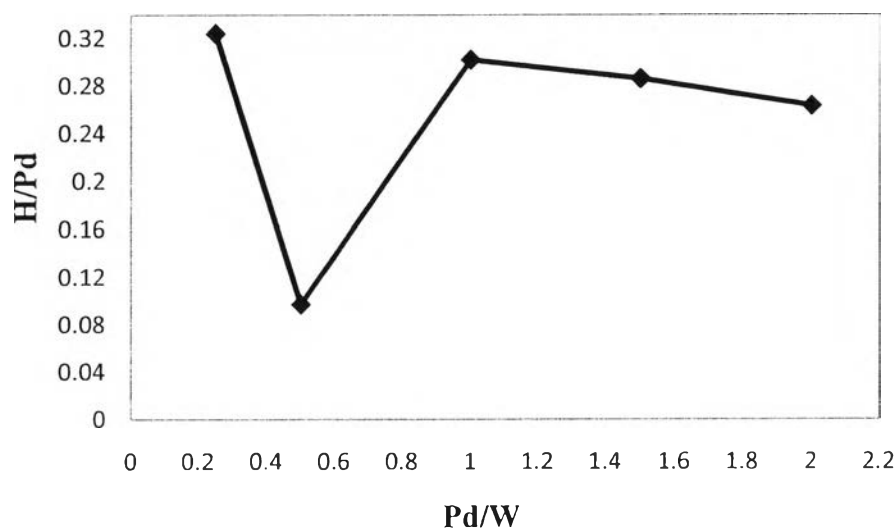
metal cluster is covered by Cu when adding more than 0.18 wt% Cu. Moreover, it can be seen that, among the tested Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, the Pd-Cu catalyst with Pd/Cu ratio of 2.0 showed the highest H/Pd which can be implied that Pd-Cu catalyst with Pd/Cu ratio of 2.0 might has the highest amount of Pd at surface.



**Figure 4.4:** H<sub>2</sub> chemisorption results of Pd-Cu supported on alumina catalysts with various Pd/Cu ratios.

#### 4.1.2.3 Pd-W Supported on Alumina Catalysts

The H<sub>2</sub> chemisorption results of Pd-W supported on alumina catalysts with various Pd/W ratios were shown in Figure 4.5. It can be seen that slightly increasing of W loading resulted the increasing of H/Pd ratio due to adding of second metal could enhance the dispersion of catalysts. At the amount of W increase up to 1.02 wt% (at Pd to W ratio 0.5), the H/Pd ratio dramatically decreases. It suggests that Pd at the surface of metal cluster is covered by W when adding second metal up to 1.02 wt%. Conversely, the addition of the amount of W up to 2.02 wt%, the H/Pd ratio increases again. It possibly due to hydrogen spillover — arises in hydrogen catalyzed reactions on supported metal catalysts. Dihydrogen molecules dissociate on the metal part of the catalyst. Some hydrogen atoms remain attached to the metal, whilst others diffuse to the support. Spillover hydrogen has often been inferred from hydrogen adsorption and reactivity studies. (Roessner, F. and Roland, U. *et al.*, 1996)

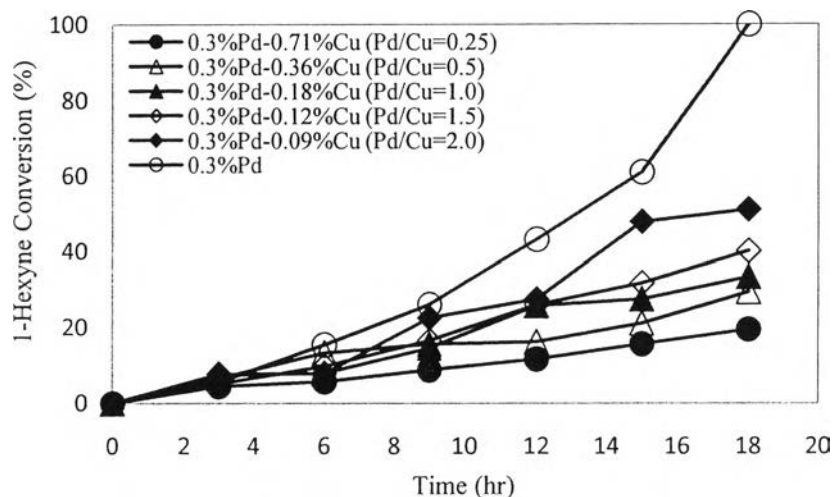


**Figure 4.5:** H<sub>2</sub> chemisorption results of Pd-W supported on alumina catalysts with various Pd/W ratios.

## 4.2 Catalytic Activity Measurement

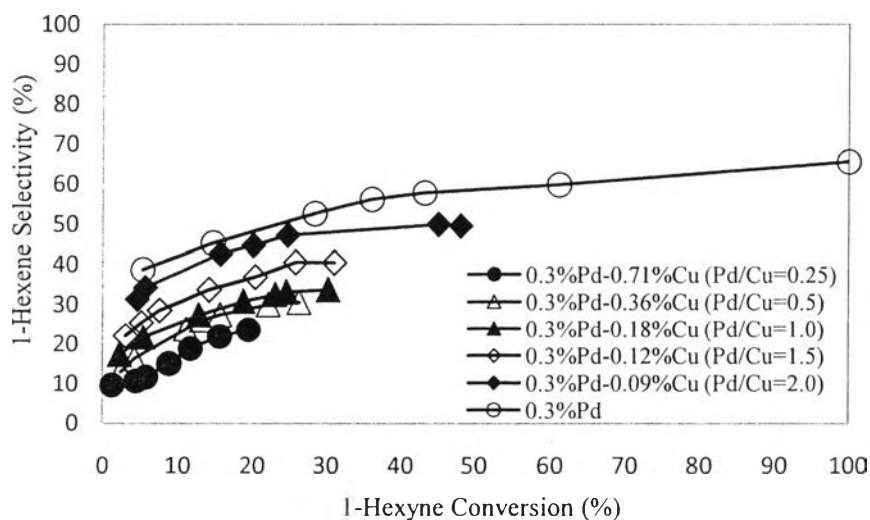
### 4.2.1 Low loaded Pd and Pd-Cu Supported on Alumina Catalysts

The activity and selectivity of low loaded Pd and Pd-Cu supported on alumina catalysts with various Pd/Cu atomic ratios were investigated for the selective hydrogenation of 1-Hexyne at 1.5 bar and 40 °C. Figure 4.6 shows the Catalytic activity of 1-Hexyne hydrogenation using 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> at various Pd/Cu ratios. It was found that 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub> gave the highest activity among the Pd-Cu catalysts. This could be due to Cu can catalyze hydrogenation reaction but it is lower active than Pd (sarkany, 1997) and 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub> has the highest amount of Pd at the surface of metal cluster which indicated by H<sub>2</sub> chemisorption results. In addition, the activity of Pd-Cu/Al<sub>2</sub>O<sub>3</sub> were decreased as increasing the amount of Cu loading because Pd at the surface of metal cluster is diluted by Cu which is lower active than Pd catalyst as confirm by H<sub>2</sub> chemisorption results.

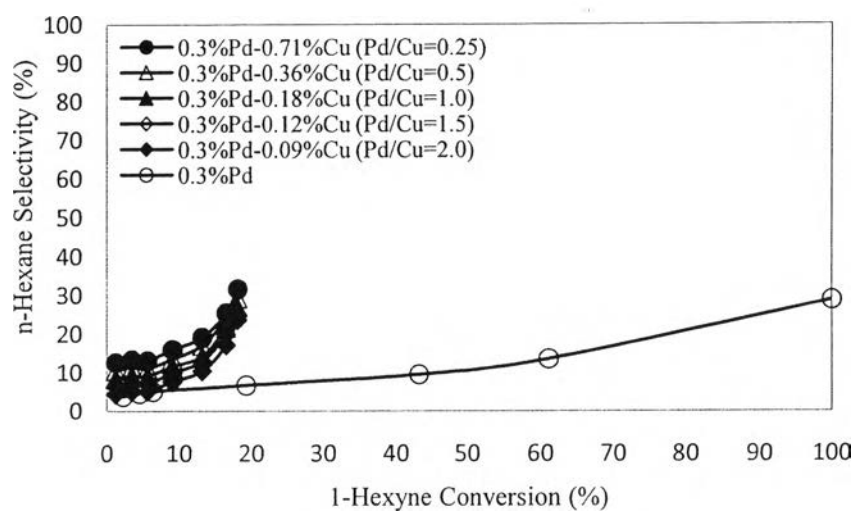


**Figure 4.6:** Catalytic activity of 1-Hexyne hydrogenation using 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> at various Pd/Cu ratios at 1.5 bar H<sub>2</sub> and 40 °C.

The 1-Hexene selectivity of 0.3% of Pd and Pd-Cu supported on alumina catalysts is shown in Figure 4.7. The result shows that 0.3% of Pd catalyst gave the highest 1-Hexene selectivity among the Pd-Cu catalysts. When focus on the Pd-Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, it can be seen that Pd-Cu/Al<sub>2</sub>O<sub>3</sub> (at Pd to Cu ratio of 2) catalyst slightly higher than the others. Furthermore, increasing amount of Cu loading causes the decreasing of the 1-Hexene selectivity. As expected, selectivity of n-hexane is also increased as shown in Figure 4.8.



**Figure 4.7:** 1-Hexene selectivity of 1-Hexyne hydrogenation using 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> at various Pd/Cu ratios at 1.5 bar H<sub>2</sub> and 40 °C.

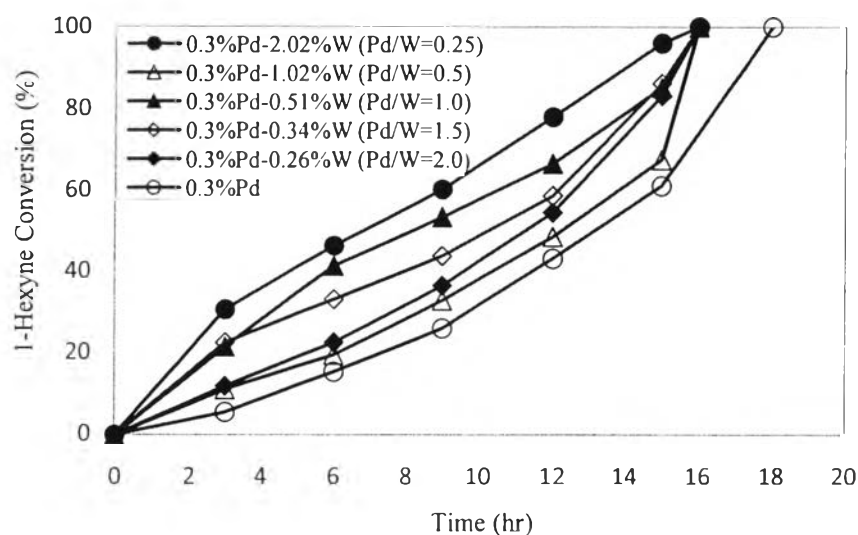


**Figure 4.8:** n-Hexane selectivity of 1-Hexyne hydrogenation using 0.3%Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Cu/Al<sub>2</sub>O<sub>3</sub> at various Pd/Cu ratios at 1.5 bar H<sub>2</sub> and 40 °C.

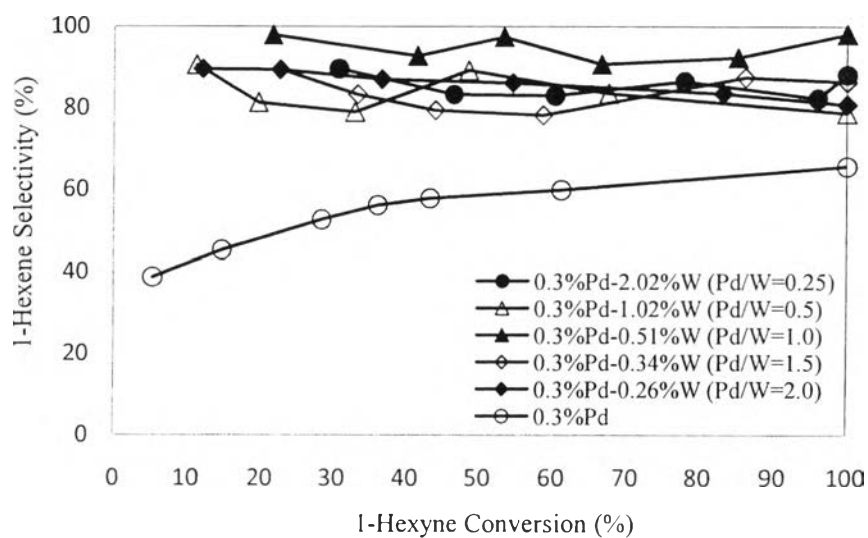
#### 4.2.2 Pd-W Supported on Alumina Catalysts

The activity and selectivity of Pd-W supported on alumina catalysts with various Pd/W atomic ratios were investigated for the selective hydrogenation of 1-Hexyne at 1.5 bar and 40 °C. Figure 4.9 shows the catalytic activity of 1-hexyne hydrogenation using Pd-W/Al<sub>2</sub>O<sub>3</sub> at various Pd/W ratios compared with 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. It can be seen that all of Pd-W/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited to be better than 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub>. It was also found that Pd-W/Al<sub>2</sub>O<sub>3</sub> (at Pd to W ratio of 0.25) gave the highest activity >Pd-W/Al<sub>2</sub>O<sub>3</sub> (ratio 1.0)> Pd-W/Al<sub>2</sub>O<sub>3</sub> (ratio 1.5)> Pd-W/Al<sub>2</sub>O<sub>3</sub> (ratio 2.0)> Pd-W/Al<sub>2</sub>O<sub>3</sub> (ratio 0.5) respectively. The catalytic activity increases when the amount of W loading is increased. For the selectivity, it can be observed that Pd-W/Al<sub>2</sub>O<sub>3</sub> (at Pd to W ratio of 1) shows the highest selectivity among the Pd-W/Al<sub>2</sub>O<sub>3</sub> catalysts. At other Pd-W ratios, increasing or decreasing of the W loading slightly changes the 1-Hexene selectivity. In addition, all ratios of Pd-W/Al<sub>2</sub>O<sub>3</sub> catalysts provide higher 1-hexyne conversion than 0.3% of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts and more importantly the selectivity toward 1-hexene is also higher. As noticed, the selectivity of 1-hexene is more than 90% for Pd/W ratio 1 at the conversion of 1-hexyne of 100%.





**Figure 4.9:** Catalytic activity of 1-Hexyne hydrogenation using Pd-W/ $\text{Al}_2\text{O}_3$  at various Pd/W ratios compared with 0.3%Pd/ $\text{Al}_2\text{O}_3$  at 1.5 bar  $\text{H}_2$  and 40 °C.



**Figure 4.10:** 1-Hexene selectivity of 1-Hexyne hydrogenation using Pd-W/ $\text{Al}_2\text{O}_3$  at various Pd/W ratios compared with 0.3%Pd/ $\text{Al}_2\text{O}_3$  at 1.5 bar  $\text{H}_2$  and 40 °C.