CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalytic Characterization

4.1.1 Temperature Programmed Reduction (TPR)

4.1.1.1 Pd Supported Alumina Catalysts

TPR profile for Pd/Al_2O_3 catayst was shown in Figure 4.1. There was a sole negative peak at around 90 °C. The nagative peak at around 70-90 °C can be attributed to the decomposition of β-Pd hydride (Lieske *et al.*, 1985). It was noticed that reduction peak did not appear because PdO can be reduced to Pd at room temperature (Batista *et al.*, 2001). Therefore, during detector stabilization which hydrogen gas was fed pass through catalyst, PdO might be completely reduced to Pd before analyzing.

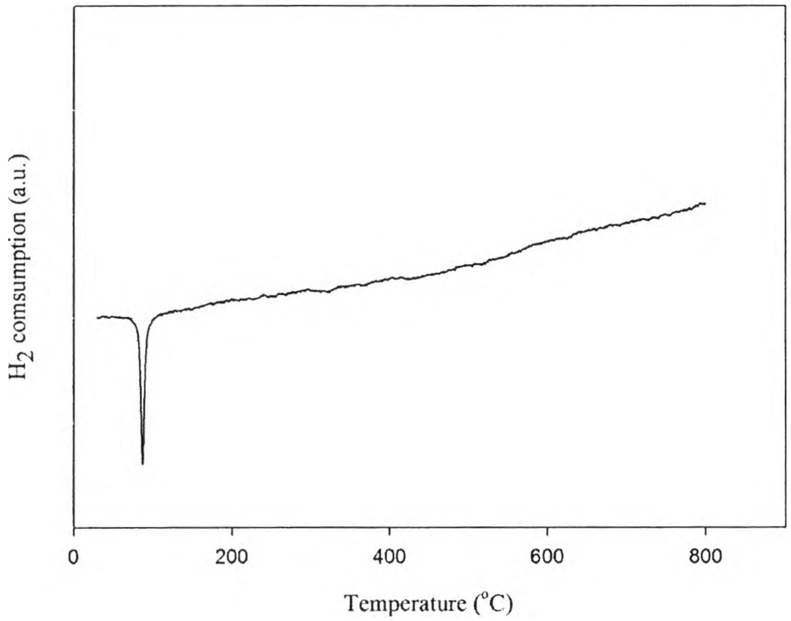

Figure 4.1 TPR profile of Pd/Al_2O_3 catalyst.

4.1.1.2 Pd-Cu Supported Alumina Catalysts

TPR profiles of Pd-Cu/Al_2O_3 with various Pd/Cu atomic ratios were shown in Figure 4.2. TPR profiles of Pd-Cu catalysts composed of 3 peaks. The negative peak at around 70-90 °C can be due to the decomposition of β-Pd hydride (Lieske *et al.*, 1985). The positive peak at around 90-110 °C can be attributed to the reduction of Cu and/or Pd from a mixed oxide (Pd_xCu_yO). The positive peak at around 220-250 °C are the reduction peak of CuO which has no interaction with Pd (Batista *et al.*, 2001). From the TPR profiles, it indicated that all of Pd-Cu catalysts composed of 3 components which are Pd, Cu which had interaction with Pd and had no interaction with Pd.

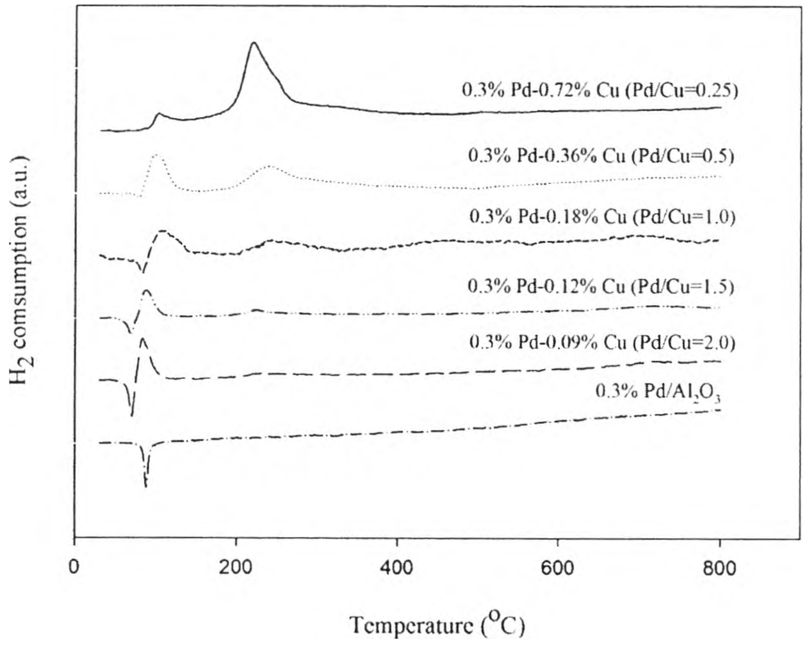

Figure 4.2 TPR profiles of 0.3% Pd/Al_2O_3 at various Cu loadings.

4.1.2 H_2 Chemisorption

H_2 chemisorption results were expressed in terms of the ratio between mole of chemisorbed H_2 and total mole of added Pd (H/Pd_t) which correspond to the amount of Pd on the surface of metal cluster of the catalysts because H_2 chemisorption can only occur on Pd under investigated condition (Furlong *et al.*, 1994). The H_2 chemisorption results of Pd catalyst were shown in Figure 4.3. The results showed that 0.1% Pd catalyst gave the highest H/Pd ratio and H/Pd ratio decreased with increasing Pd loading. It can suggest that amout of Pd at the surface of metal cluster, which correspond to the dispersion of catalyst, decrease with increasing Pd loading.

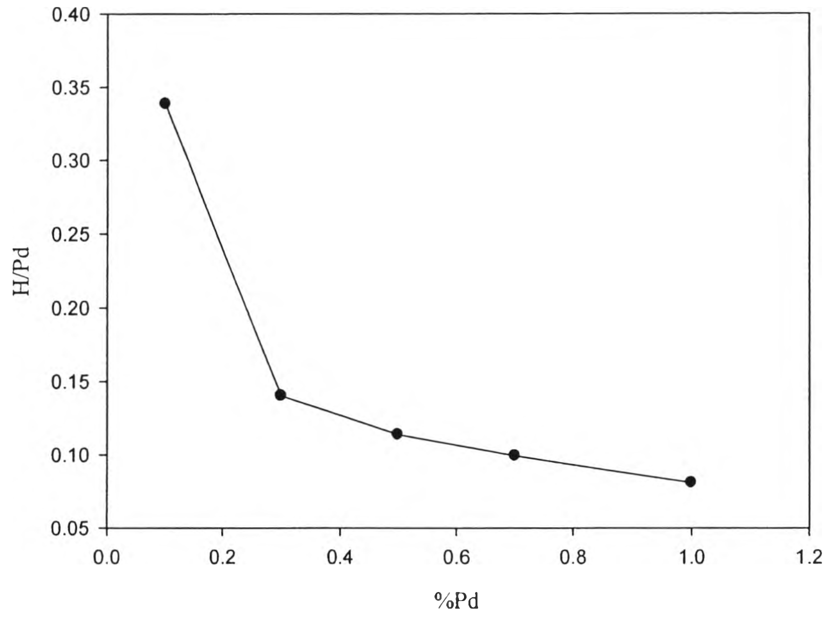

Figure 4.3 H_2 chemisorption results of Pd catalysts with various Pd loading.

The H_2 chemisoprtion results of Pd-Cu catalysts were shown in Figure 4.4. The result showed that H/Pd_t ratio slightly changed when adding low amount of Cu. It indicated that Pd at the surface of metal cluster was not much diluted by added Cu. H/Pd_t ratio dramatically decrease when adding Cu more than 0.18 wt% Cu. It indicated that Pd at the surface of metal cluster was covered by Cu when adding more than 0.18 wt% Cu. Moreover, it can be seen that the Pd-Cu catalyst with Pd/Cu ratio of 1.5 showed the highest H/Pd_t which can be implied that Pd-Cu catalyst with Pd/Cu ratio of 1.5 might has the highest amount of Pd at surface of metal cluster.

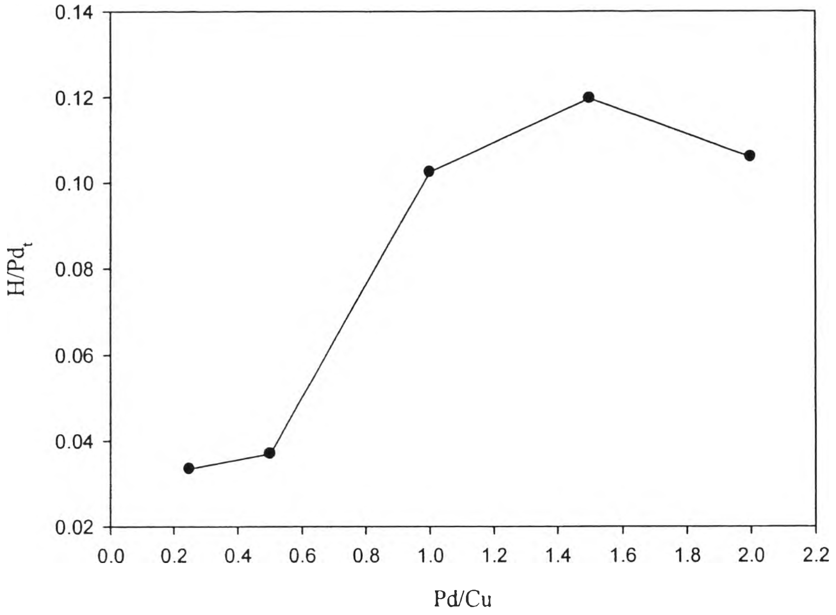

Figure 4.4 H_2 chemisorption results of Pd-Cu catalysts with various Pd/Cu ratios.

4.2 Catalytic Activity Measurement

4.2.1 Pd Supported Alumina Catalysts

The catalytic activity measurement of Pd catalysts were studied in the selective hydrogenation of vinylacetylene at 35 °C and 4.5 bar. The catalytic activity and selectivity of various amount of loaded Pd (0.1, 0.3, 0.5, 0.7, 1.0 wt%) were shown as Figure 4.5, 4.6 and 4.7. The results showed that vinylacetylene conversion of Pd catalysts, which had different loaded Pd, reached 100% at different reaction time. 1.0 wt% Pd/Al_2O_3 reached 100% vinylacetylene conversion first followed by 0.7%, 0.5%, 0.3% and 0.1% Pd/Al_2O_3 respectively (Figure 4.5). This results suggest that activity for vinylacetylene hydrogenation increase with increasing amount of loaded Pd. For selectivities, 1,3-butadiene selectivity of Pd catalysts were constant at low vinylacetylene conversion and it started decreasing around 70% vinylacetylene conversion (Figure 4.6). 1-Butene selectivity slightly increased at low vinylacetylene conversion and above 70% vinylacetylene conversion, it dramatically increased (Figure 4.7). Within the studied Pd loading range, it was found that 0.3% of Pd catalyst gave the highest 1,3-butadiene selectivity and the lowest 1-butene selectivity.

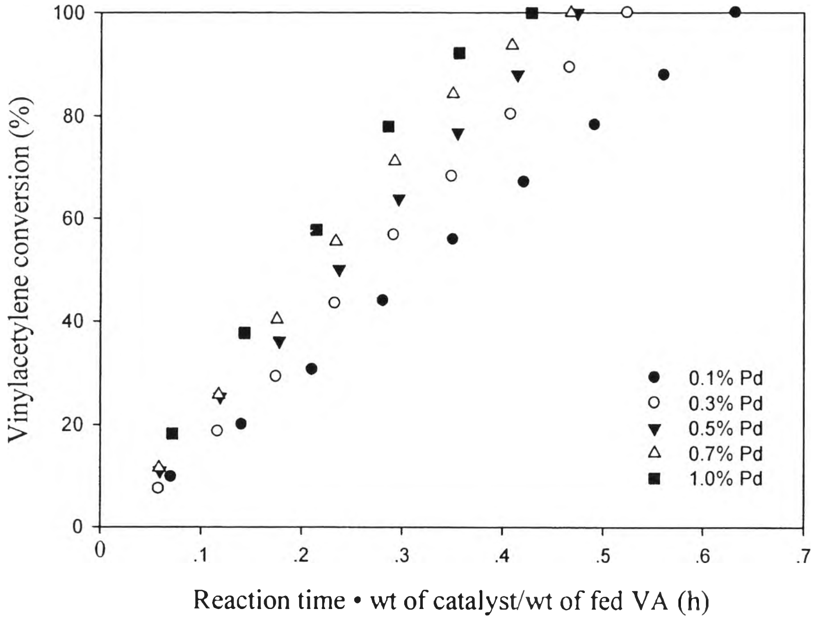

Figure 4.5 Catalytic activity of Pd/Al_2O_3 at various Pd loadings at 35 °C and 4.5 bar H_2.

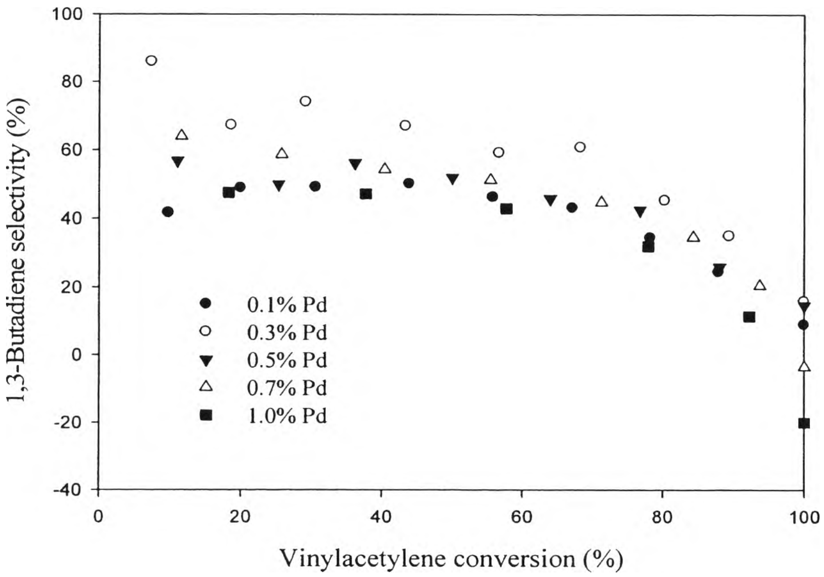

Figure 4.6 1,3-Butadiene selectivity from hydrogenation of vinylacetylene using Pd/Al_2O_3 at various Pd loadings at 35 °C and 4.5 bar H_2.

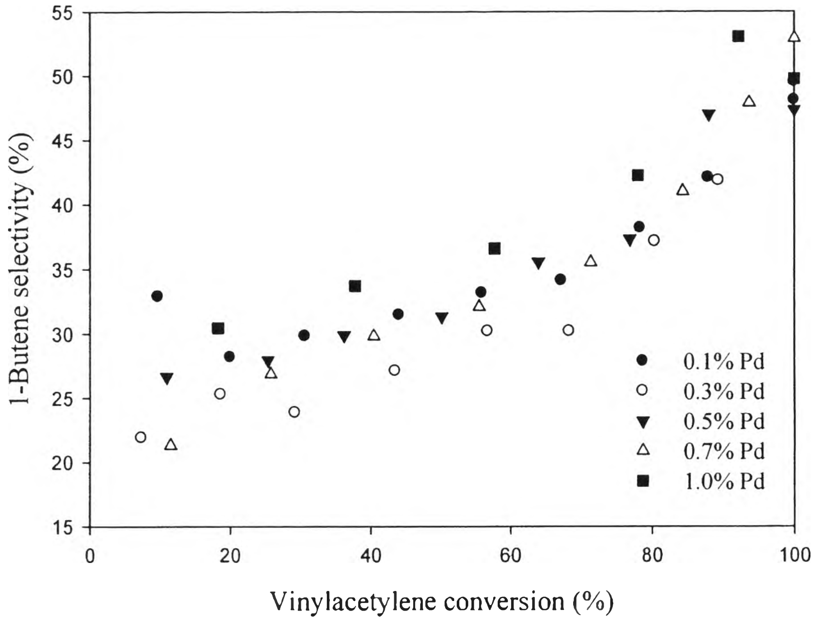

Figure 4.7 1-Butene selectivity from hydrogenation of vinylacetylene using Pd/Al_2O_3 at various Pd loadings at 35 ^oC and 4.5 bar H_2.

4.2.2 Pd-Cu Supported Alumina Catalysts

From the previous work, 0.3 wt% Pd loading gave the best 1,3-butadiene selectivity within the range of Pd loadings investigated. Therefore, Cu was added in the range of 0.09 - 0.72 wt% to the catalyst with 0.3% Pd. The activity and selectivity of Pd-Cu catalyst with various Pd/Cu atomic ratios were investigated in the selective hydrogenation of vinylacetylene at 35 ^oC and 4.5 bar. Figure 4.8 shows the catalytic activity of Pd-Cu catlysts. It was found that activity of Pd-Cu catalysts were different from Pd catalyst. The acitivity increased in order of 0.3% Pd-0.72% Cu/Al_2O_3 (Pd/Cu=0.25) < 0.3% Pd-0.36% Cu/Al_2O_3 (Pd/Cu=0.5) < 0.3% Pd/Al_2O_3< 0.3% Pd-0.09% Cu/Al_2O_3 (Pd/Cu=2.0) < 0.3% Pd-0.18% Cu/Al_2O_3 (Pd/Cu=1.0) < 0.3% Pd-0.12% Cu/Al_2O_3 (Pd/Cu=1.5). This could be due to Cu can catalyze hydrogenation reaction but it is lower active than Pd (Sarkany., 1997). Therefore, the addition of Cu to Pd catalyst is an increase of active site which cause to increase the activity in vinylacetylene hydrogenation to higher than activity of 0.3% Pd catalyst. However, the addition of high amount of Cu causes the activity of Pd-Cu catalyst to decrease because Pd at the surface of metal cluster is diluted by Cu which is lower active than Pd catalyst as confirmed by H_2 chemisorption results. Moreover, the Pd-Cu catalyst with Pd/Cu ratio of 1.5 exhibited the highest activity. Because it has the highest amount of Pd at the surface of metal cluster which was indicated by H_2 chemisorption results.

The 1,3-butadiene and 1-butene selectivity of Pd-Cu catalysts were shown in Figure 4.9 and 4.10. It can be seen that 1,3-butadiene of all Pd-Cu catalysts is slightly lower than Pd catalyst and the Pd-Cu catalysts show the slightly higher 1-butene selectivity than Pd catalyst.

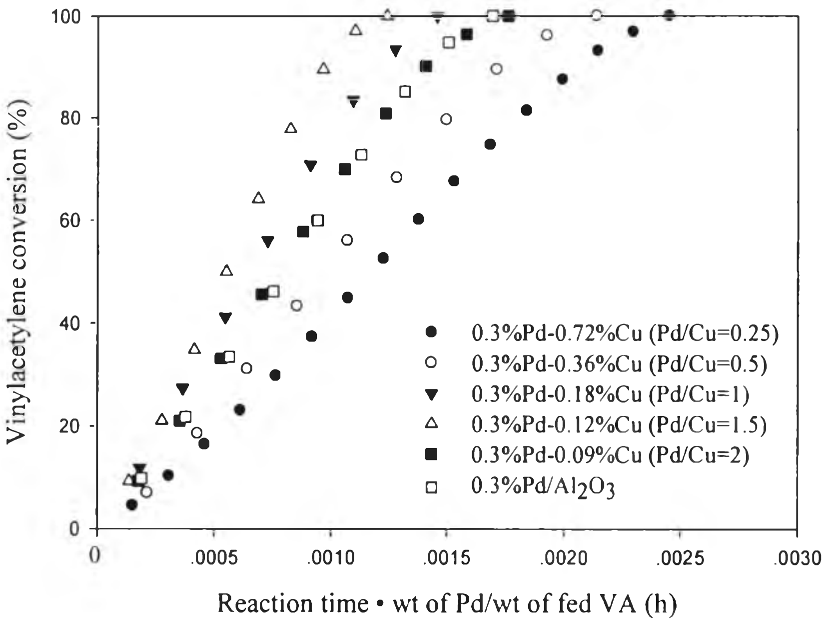

Figure 4.8 Catalytic activity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 35 °C and 4.5 bar H_2.

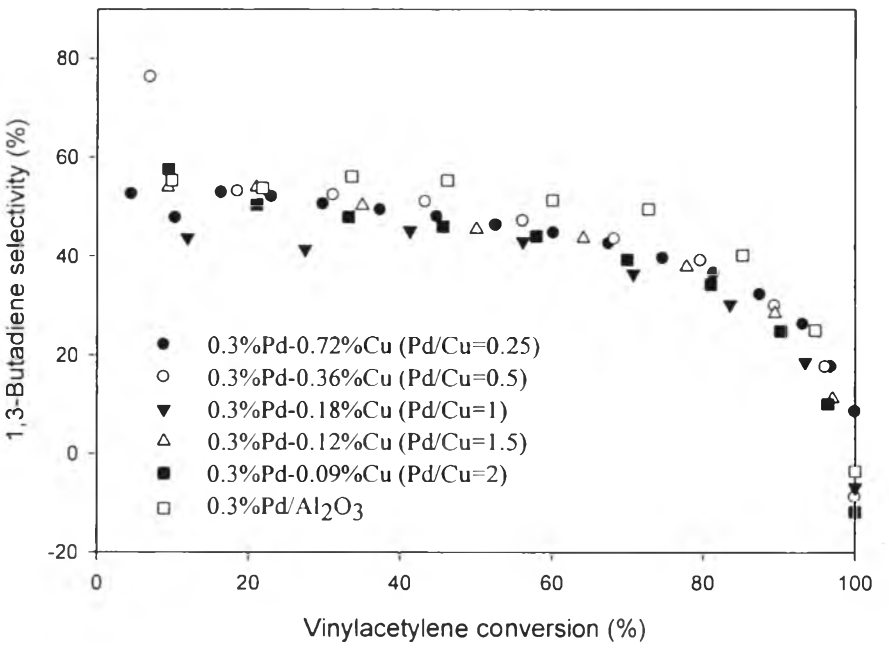

Figure 4.9 1,3-Butadiene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 35 °C and 4.5 bar H_2.

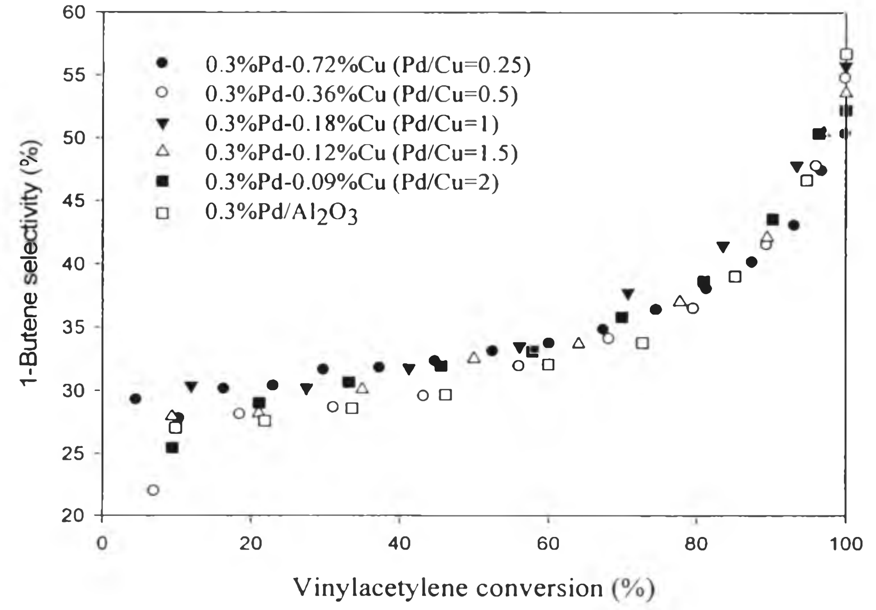

Figure 4.10 1-Butene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 at various Pd/Cu ratios at 35°C and 4.5 bar H_2.

The activity and selectivity of Pd-Cu catalysts with Pd/Cu ratio of 1.5 were studied at different temperatures and pressures.

To study the effect of reaction temperature on the vinylacetylene hydrogenation, The reaction temperature was varied from 27 °C to 43 °C. The results were shown in Figure 4.11, 4.12 and 4.13. It can be seen that catalytic activity increases with increasing temperature but the reaction temperatue has no influence on both 1,3-butadiene and 1-butene selectivity (Figure 4.12 and 4.13). Because the reaction rate constant relate with reaction temperature according to the Arrhenius relationship. So, higher reaction temperature would increase rate of reaction but it did not significantly change in 1,3-butadiene selectivity because the studied reaction temperature range may be too narrow to significantly change in selectivity.

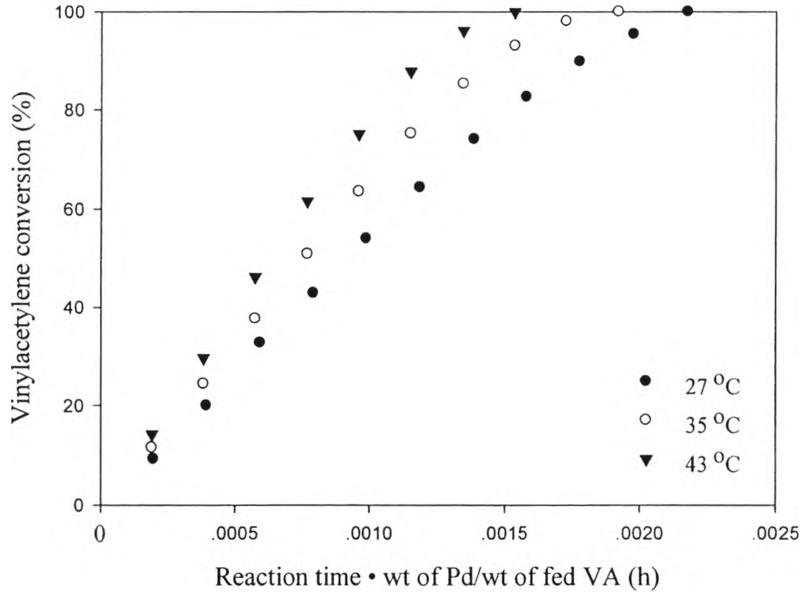

Figure 4.11 Catalytic activity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 27, 35, 43 °C and 4.5 bar H_2.

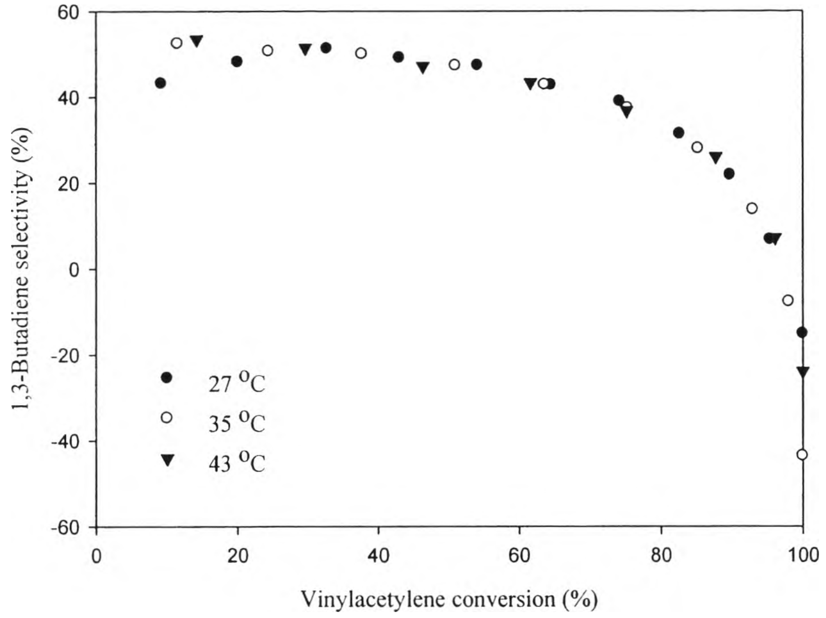

Figure 4.12 1,3-Butadiene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 27, 35, 43 °C and 4.5 bar H_2.

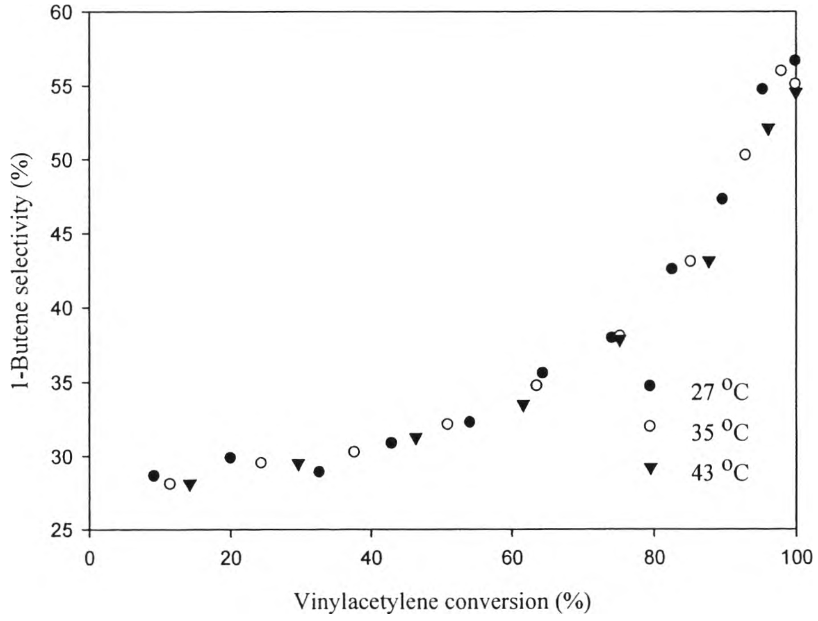

Figure 4.13 1-Butene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 27, 35, 43 °C and 4.5 bar H_2.

To study the effect of H_2 pressure on the vinylacetylene hydrogenation, the H_2 pressure was varied from 3.5 bar to 5.5 bar. The catalytic activity and selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 under various H_2 pressures were shown in Figure 4.14, 4.15 and 4.16. When H_2 pressure was increased, the catalytic activity and 1-butene increased while 1,3-butadiene selectivity decreased. Because H_2 is reactant in hydrogenation reaction and H_2 pressure is directly proportional to rate of reaction. So higher H_2 pressure lead to increase hydrogenation rate and over-hydrogenation which cause decreasing in 1,3-butadiene selecitivity.

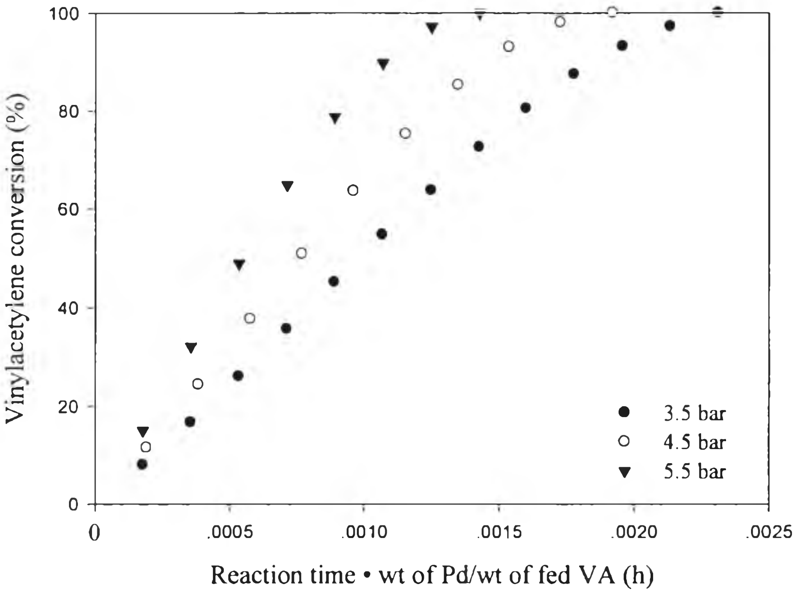

Figure 4.14 Catalytic activity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 35 °C and 2.5, 3.5, 4.5 bar H_2.

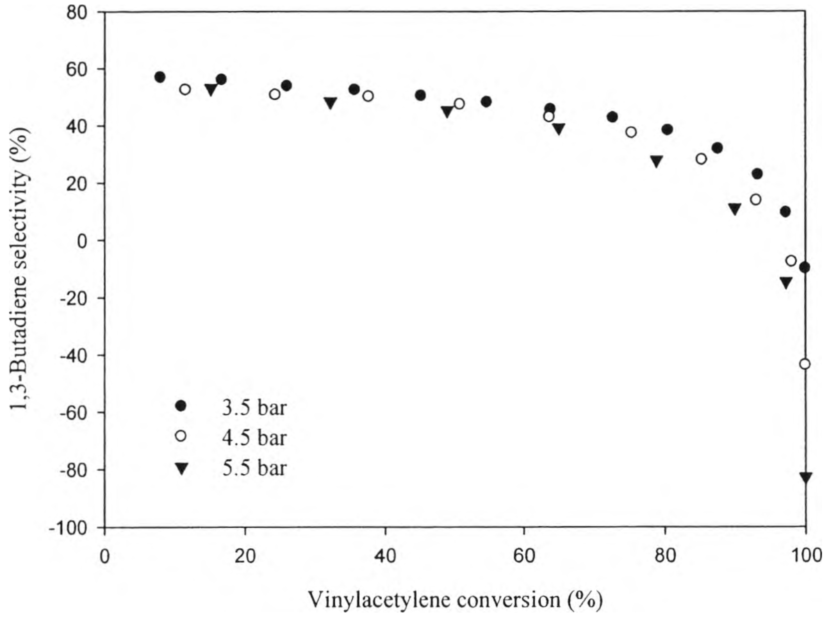

Figure 4.15 1,3-Butadiene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 35 °C and 2.5, 3.5, 4.5 bar H_2.

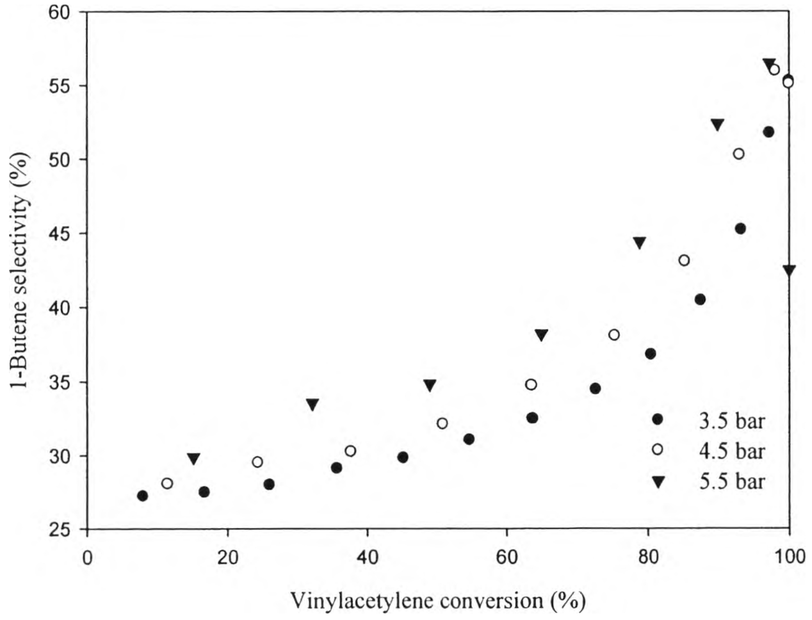

Figure 4.16 1-Butene selectivity of vinylacetylene hydrogenation using Pd-Cu/Al_2O_3 with Pd/Cu ratio of 1.5 at 35 °C and 2.5, 3.5, 4.5 bar H_2.