CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalytic Characterization

4.1.1 Temperature Program Reduction (TPR)

This method is used to evaluate the reduction of palladium and manganese species on the alumina catalyst surface by hydrogen and reveal the temperature at which the reduction of each species occurs.

4.1.1.1 Pd Supported on Alumina Catalyst

Lederhos *et al.* (2011) suggested that the TPR profile of the Pd monometallic catalyst had a main hydrogen consumption peak at low temperature. This peak can be ascribed to the reduction of PdO to Pd^0 and the formation of palladium hydrides. The catalyst also has a negative peak after reduction at 113 $^{\circ}$C (Ngamsom *et al.*, 2004) which can be corresponded to the desorption of the hydrogen weakly adsorbed on palladium, as well as, the decomposition of the palladium hydride formed on the metallic palladium (Hong *et al.*, 2014). From Figure 4.1, it can be seen that there has two peaks. The main hydrogen consumption peak at around 70 $^{\circ}$C which can be attributed to the reduction of PdO species on the alumina support surface and a negative peak at around 120 $^{\circ}$C which can be attributed to the desorption of the hydrogen weakly absorbed on palladium or the decomposition of the palladium hydride formed on the palladium.

4.1.1.2 Pd-Mn Supported on Alumina Catalysts

Álvarez-Galván *et al.* (2004) suggested that the TPR profiles of Pd-Mn catalyst had the three H_2 consumption peaks. The first peak is at temperature about 100 $^{\circ}$C. The intensity of this peak increases with increasing Pd content due to the reduction of PdO to Pd^0. The second peak is at temperature around 300-320 $^{\circ}$C and relates to the reduction of Mn^{3+} and Mn^{4+} ions to the Mn_3O_4 phase ($MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$). The last peak together with shoulder are at around 390-430 °C and are designated to the reduction of Mn_3O_4 which interacts with the alumina surface to the MnO. Moreover, the comparison of TPR profiles of the Pd-

Mn sample and its Pd-free Mn counterpart indicates that the two reduction steps of the manganese oxides are shifted to slightly lower temperatures in the Pd-containing sample due to the catalytic effect of Pd^0 on the reduction of manganese oxides via spillover during the TPR process or to the increase in the oxygen mobility in the Mn_3O_4 phase. From Figure 4.2, it can be seen that the main hydrogen consumption peak at around 80 °C which can be attributed to the reduction of PdO species on the alumina support surface and the second peak is at around 320-330 °C and the last peak is at around 440-450 °C. Moreover, the first peak of $Pd-Mn/Al_2O_3$ (Pd/Mn = 1.0) is more intensive than the first peak of the other $Pd-Mn/Al_2O_3$ catalysts which relates to more active than the other $Pd-Mn/Al_2O_3$ catalysts. Besides, it can be seen that the first peak of Mn/Al_2O_3 catalyst is at around 340-350 °C and the second peak is at around 460-470 °C.
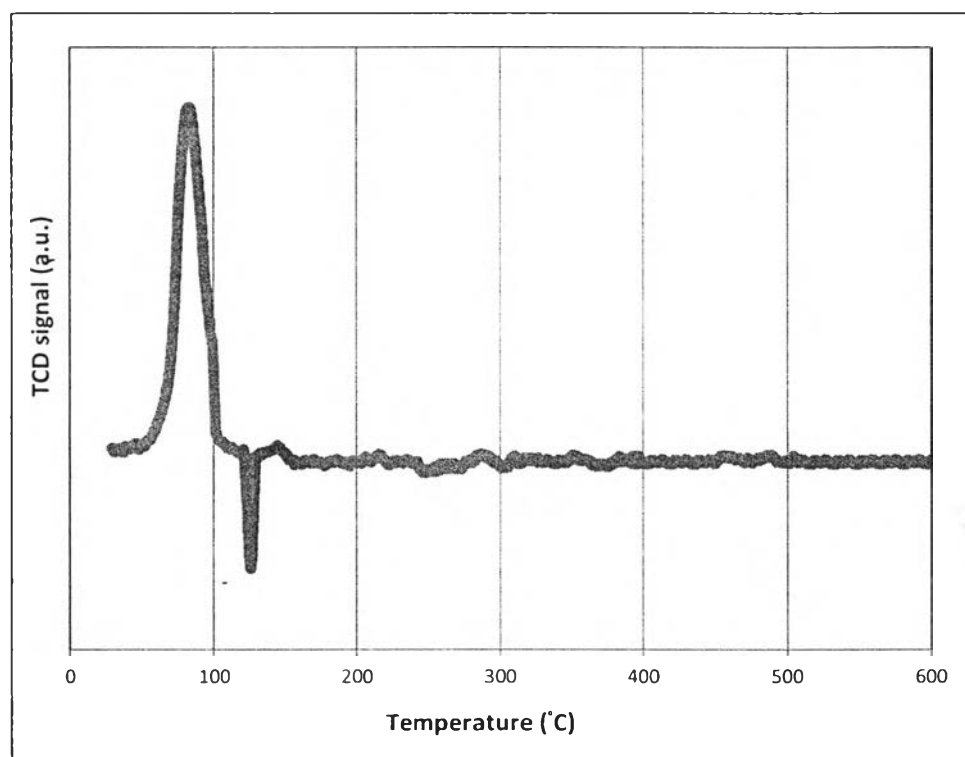
Figure 4.1 TPR profile of 0.3 wt% Pd/Al_2O_3 catalyst.
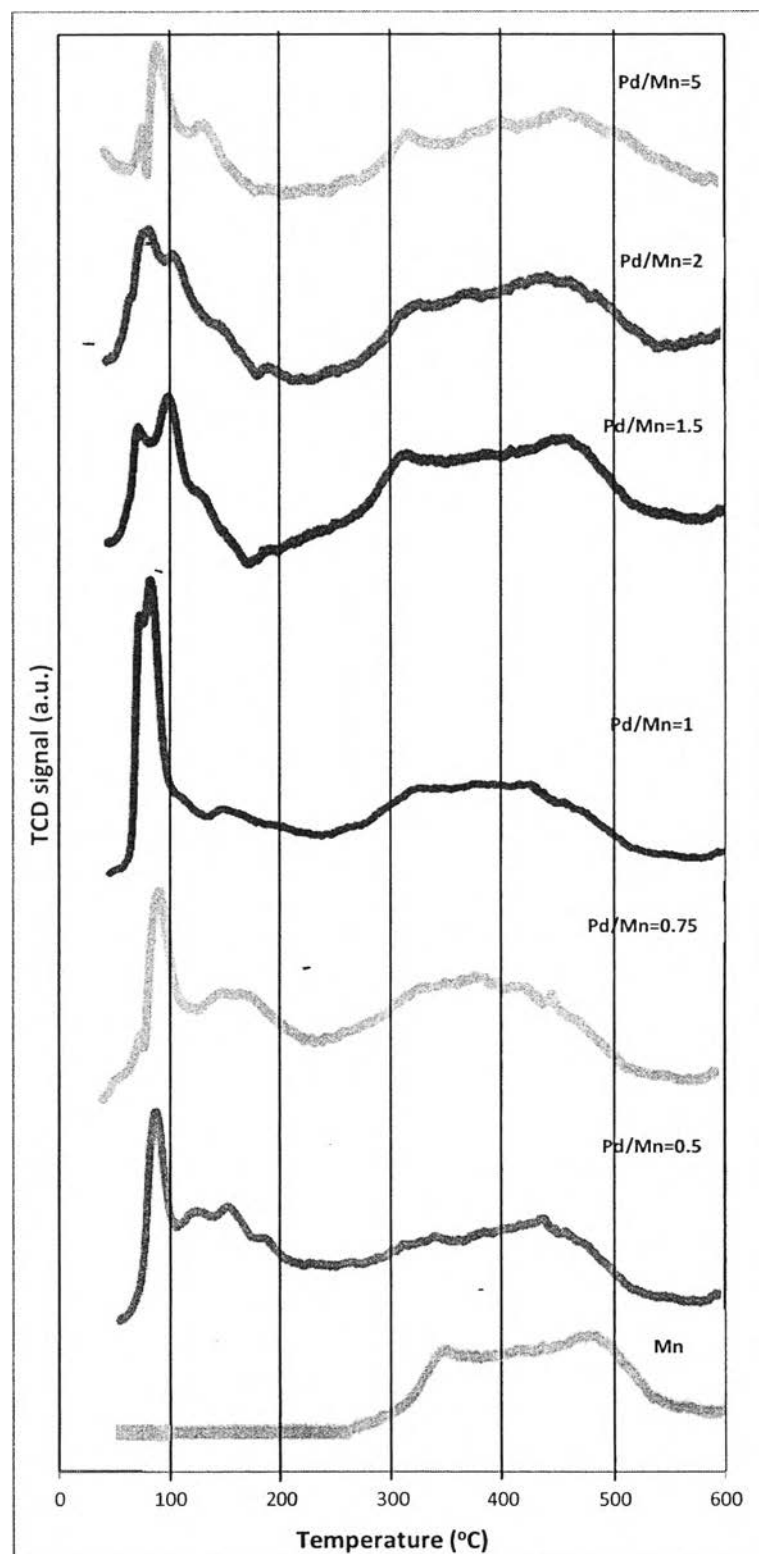
Figure 4.2 TPR profiles of Mn/Al_2O_3 and 0.3 wt% Pd/Al_2O_3 catalysts at various Mn loadings.

Comparing these profiles with that obtained for Pd/Al$_2$O$_3$ catalyst, in the Pd-Mn/Al$_2$O$_3$ catalysts there is a shift of PdO reduction peak to slightly higher temperature and a shift of MnO$_2$ and Mn$_3$O$_4$ reduction to lower temperature. It indicates that the presence of Mn modifies the reducibility of Pd. In general, the shift to higher temperature may be corresponded to an interaction or electron transfer between Pd and Mn (Maccarone *et al.*, 2012). Besides, the disappearance of the PdH phase in Pd-Mn/Al$_2$O$_3$ catalysts considerably decreases the alkynes hydrogenation rate to alkanes, thus increasing the selectivity to alkenes. It is well known that in the case of alkyne hydrogenations on supported Pd catalysts, the hydride phase may act as a hydrogen source that promotes overhydrogenation, with a consequent decrease in the selectivity to alkene formation (Lederhos *et al.*, 2010).

4.1.2 Hydrogen Chemisorption

If the metal dispersion on the support increases, not only the number of active site that is effective to reaction increases but also the contribution of atoms at the corner or edge of metal particle increases, or reaction activity or selectivity changes due to interaction between metal and support. In case of rare metal catalyst, it is important to find out metal dispersion because rare metal is expensive. It is important to increase the activity with as small amount of metal as possible. Hydrogen chemisorption results are shown in terms of the ratio between mole of chemisorped H$_2$ and total mole of added Pd (H/Pd) which relate to the amount of Pd on the catalyst surface of the metal cluster of the catalysts because H$_2$ can only chemisorp on Pd under investigated condition (Furlong *et al.*, 1994).

4.1.2.1 Pd Supported on Alumina Catalyst

The hydrogen chemisorption result of 0.3 wt% Pd catalyst is equal to 0.3381. From the results show that 0.3 wt% Pd catalyst (100 mol% Pd) gives the highest H/Pd ratio when it is compared with Pd-Mn/Al$_2$O$_3$ in Figure 4.3. It indicates that 0.3 wt% Pd catalyst may has the highest amount of Pd on the alumina surface.

4.1.2.2 Pd-Mn Supported on Alumina Catalysts

The hydrogen chemisorption results of Pd-Mn supported on alumina catalysts at various Mn loadings are shown in Figure 4.3. The results

indicate that the H/Pd ratios of Pd/Mn = 0.5, 0.75 and 1.0 (mol% Pd = 33.3, 42.9 and 50.0, respectively) are slightly decreased with increasing of Mn concentration. In contrast, the increase of Mn loadings of Pd/Mn = 1.5, 2.0, 5.0 (mol% Pd = 60.0, 66.7 and 83.3, respectively) result the decrease in H/Pd ratio. Moreover, it can be seen that the Pd-Mn/Al$_2$O$_3$ catalyst (Pd/Mn = 1.0) shows a little higher H/Pd ratio than the other tested Pd-Mn/Al$_2$O$_3$ catalysts which can be implied that the amount of Pd on the alumina surface of Pd-Mn/Al$_2$O$_3$ catalyst (Pd/Mn = 1.0) may be higher than the other tested Pd-Mn/Al$_2$O$_3$ catalysts, but the H/Pd ratio of Pd-Mn/Al$_2$O$_3$ catalyst (Pd/Mn = 1.0) along with the other tested Pd-Mn/Al$_2$O$_3$ catalysts are lower than H/Pd ratio of the Pd/Al$_2$O$_3$ catalyst because increasing the Mn concentration may block some of the Pd (Karavanov *et al.*, 1995).
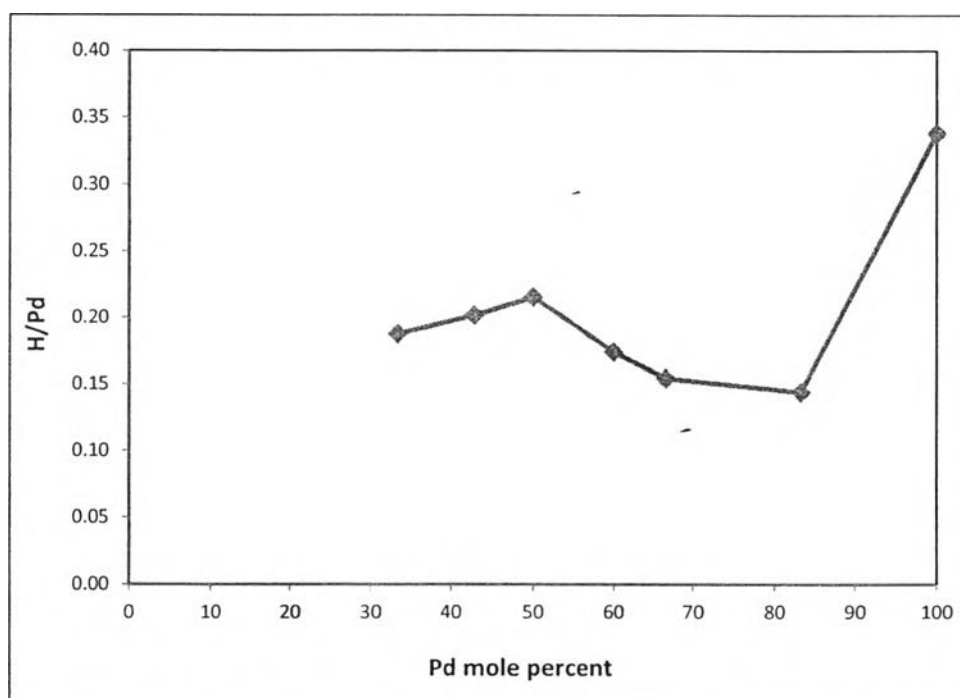
Figure 4.3 H$_2$ chemisorption results of 0.3 wt% Pd/Al$_2$O$_3$ catalysts at various Mn loadings.

4.1.3 X-ray Photoelectron Spectroscopy (XPS)

The XPS results for the 0.3 wt% Pd/Al_2O_3 catalysts at various Mn loadings 0.3 wt% Pd/Al_2O_3 catalysts at various Mn loadings are shown in Figure 4.4 and the binding energies of Pd $3d_{5/2}$ are listed in Table 4.1. From Figure 4.4, the Pd $3d_{5/2}$ spectrum of Pd/Al_2O_3 catalyst has a peak at 335.9 eV that corresponds to PdO (Naumkin et al., 1996). In the case of the $Pd-Mn/Al_2O_3$ catalysts, it can be seen that the increase in the Pd binding energy of all $Pd-Mn/Al_2O_3$ catalysts from Pd/Al_2O_3 catalyst can be attributed to an electron transfer from Pd to Mn or more Pd^{n+} electron-deficient species and the Pd binding energy of the $Pd-Mn/Al_2O_3$ catalysts are increased with Mn loadings. In other words, it may be more interaction between Pd and Mn because the more Mn is loaded, the more Mn interacts with Pd. In general, when a metal or a metal oxide phase is deposited on the support surface, where it develops a strong metal (oxide)-support interaction, the binding energy of core-levels of the supported element (Pd 3d in this work) is shifted toward higher binding energy with respect the bulk oxide (Álvarez-Galván et al., 2004).

**Table 4.1** Binding energy (eV) of core-level of the catalysts

Catalysts	Pd $3d_{5/2}$
Pd/Al_2O_3	335.9
$Pd-Mn/Al_2O_3$ (Pd/Mn = 5.0)	336.4
$Pd-Mn/Al_2O_3$ (Pd/Mn = 2.0)	336.5
$Pd-Mn/Al_2O_3$ (Pd/Mn = 1.0)	336.6
$Pd-Mn/Al_2O_3$ (Pd/Mn = 0.5)	337.2

4.2 Catalytic Activity Measurement

The activity and selectivity of 0.3 wt% Pd and Pd-Mn supported on alumina catalysts at various Mn loadings (0.5, 0.75, 1.0, 1.5, 2.0 and 5.0) are investigated for the selective hydrogenation of 1-hexyne at 40 °C and 1.5 bar. Figure 4.5 and Figure
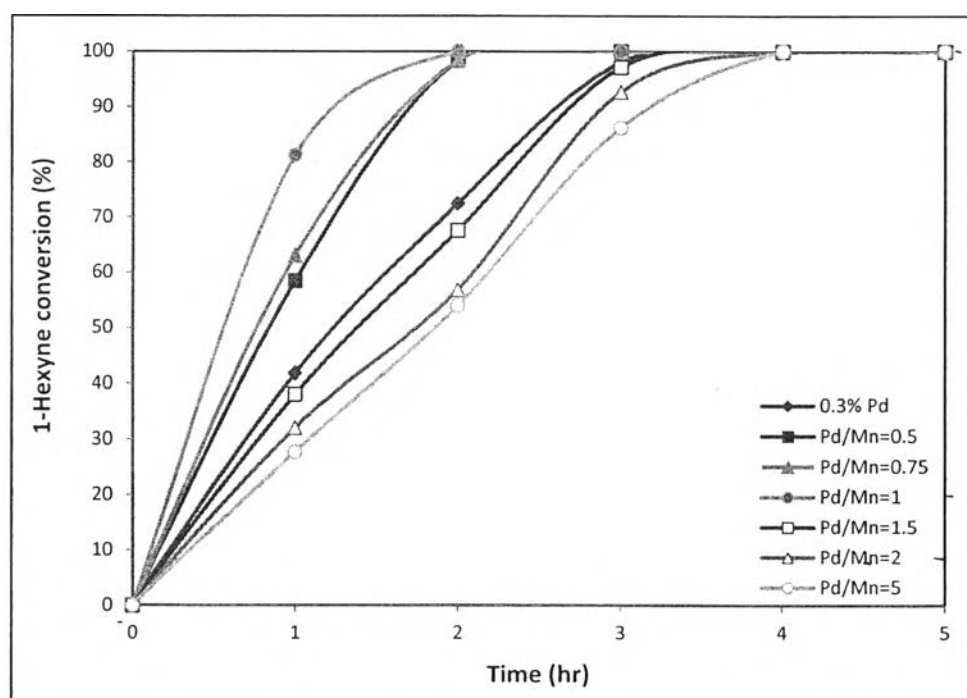
4.6 are shown the catalytic activity for the hydrogenation of 1-hexyne at 40 $^{\circ}$C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at various Mn loadings.
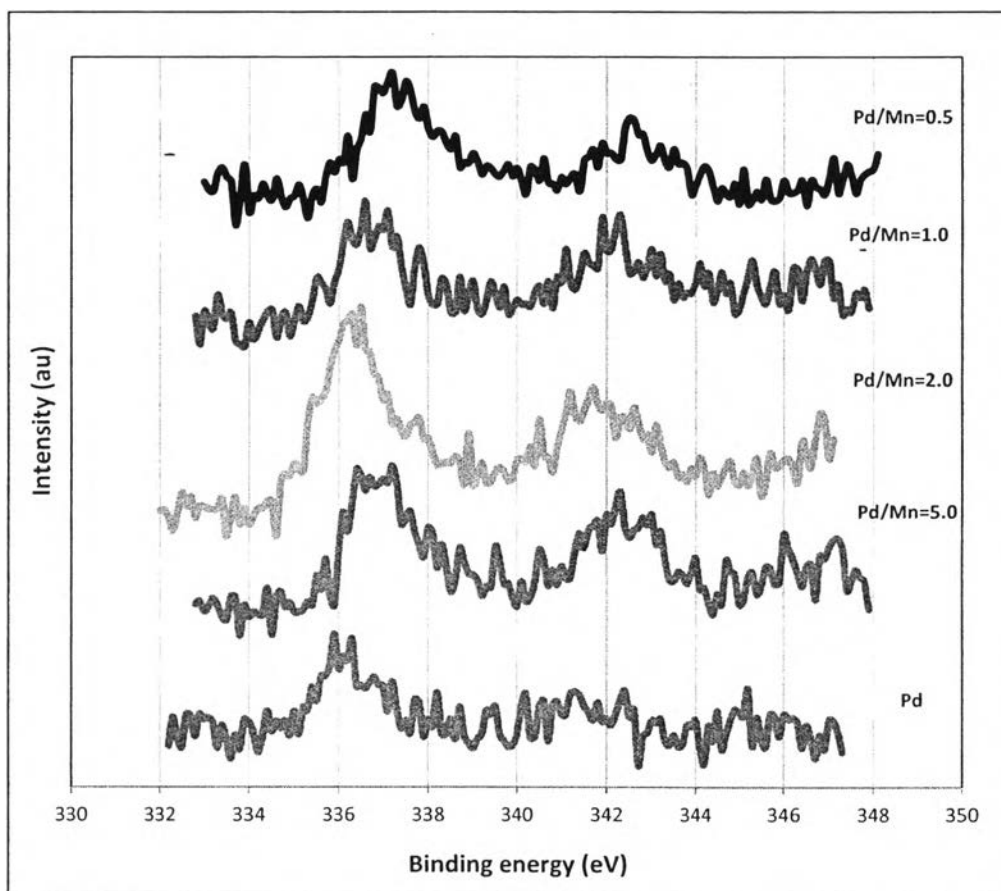
Figure 4.4 XPS results for the 0.3 wt% Pd/Al_2O_3 catalysts at various Mn loadings.

From the results, it can be observed that the hydrogenation activity is significantly improved when Mn is doped on the Pd/Al_2O_3 catalysts (Pd/Mn = 0.5, 0.75 and 1.0). The 1-hexyne conversion of $Pd-Mn/Al_2O_3$ (Pd/Mn 0.5, 0.75 and 1.0) catalysts are over 98 % at 2 h reaction time. In addition, The $Pd-Mn/Al_2O_3$ catalyst (Pd/Mn = 1.0) provides the highest conversion among the tested Pd-Mn catalysts as it has the highest amount of Pd at the surface of metal cluster which is indicated by the highest H_2 chemisorption result among the other $Pd-Mn/Al_2O_3$ catalysts. The conversion of $Pd-Mn/Al_2O_3$ (Pd/Mn = 0.5, 0.75) catalysts are decreased from $Pd-Mn/Al_2O_3$ (Pd/Mn = 1.0) catalyst which can be indicated that the increasing of Mn concentration may

block some of the active phase (Karavanov *et al.*, 1995). In contrast, the conversion of Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1.5, 2.0 and 5.0) catalysts are slightly decreased with reducing Mn loadings and are less active than Pd/Al$_2$O$_3$ catalyst. The results of all tested Pd-Mn/Al$_2$O$_3$ catalysts are related to the H$_2$ chemisorption results in Figure 4.3 because the catalytic conversion of all tested Pd-Mn/Al$_2$O$_3$ catalysts are increased with increasing of H$_2$ chemisorption. The rank of 1-hexyne conversion found is: Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1.0) > Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 0.75) > Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 0.5) > Pd/Al$_2$O$_3$ > Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1.5) > Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 2.0) > Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 5.0). As reported by Suriyaphaparkorn (2013), the Pd-Mn/Al$_2$O$_3$ catalysts are more active than both Pd-Cu/Al$_2$O$_3$ and Pd-W/Al$_2$O$_3$ catalysts when compare in range of 1-5 h reaction time.
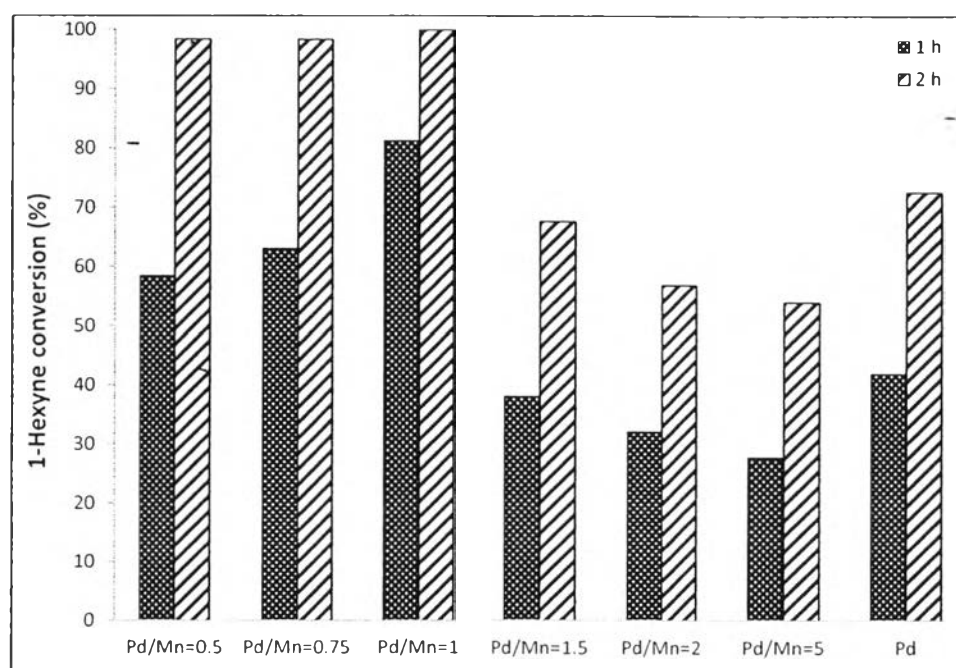

Figure 4.5 Catalytic conversion as a function of reaction time for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings.

The 1-hexene selectivity for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings is shown in Figure 4.7 and Figure

4.8. The results indicate that the Pd-Mn/Al$_2$O$_3$ catalysts are more selective than Pd/Al$_2$O$_3$ catalyst. Increasing amount of Mn loadings causes the slight decrease of the 1-hexene selectivity. The selectivity to 1-hexene of Pd-Mn/Al$_2$O$_3$ catalysts are all
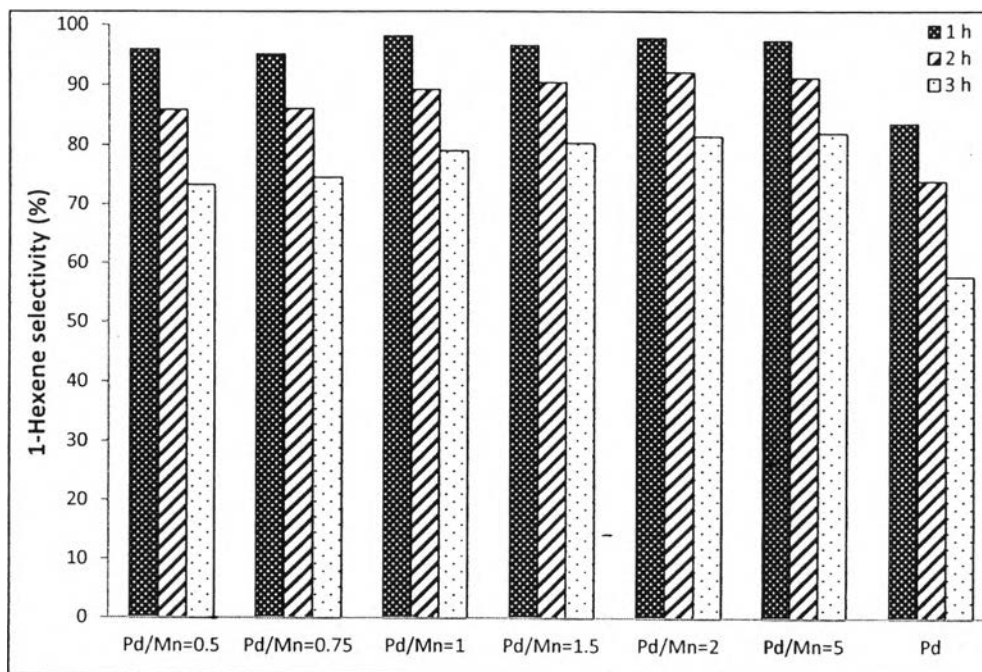

Figure 4.6 Catalytic conversion for the hydrogenation of 1-hexyne at 40 °C, 1.5 bar, and 1-2 h reaction time over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings.

over 95 % at 1 h reaction time and the decrease in selectivity can be observed as the reaction progressed. Simultaneously, the small increase in the selectivity to n-hexane is observed. Moreover, The Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 5.0) catalyst is slightly more selective than other Pd-Mn/Al$_2$O$_3$ catalysts. The 1-hexene selectivity of all tested Pd-Mn/Al$_2$O$_3$ catalysts are related to the XPS results in Figure 4.4 because the 1-hexene selectivity of all tested Pd-Mn/Al$_2$O$_3$ catalysts are increased with decreasing of Pd binding energy results. In other words, the interaction between Pd and Mn affects on the 1-hexene selectivity. It is known that electron density transfer from the hydrocarbon molecule on the metal atom occurs during the interaction of unsaturated hydrocarbons with transition metals. In this instance, the decrease in electron density on Pd will probably contribute to the increase in the bond strength of chemisorbed 1-

hexene and thus will lead to a decrease in 1-hexene selectivity. Consequently, the low 1-hexene selectivity of Pd/Al_2O_3 catalyst is due to a stronger chemisorption of 1-hexene on the electron-deficient Pd clusters. The rank of 1-hexene selectivity found is: $Pd-Mn/Al_2O_3$ (Pd/Mn = 5.0) > $Pd-Mn/Al_2O_3$ (Pd/Mn = 2.0) > $Pd-Mn/Al_2O_3$ (Pd/Mn = 1.5) > $Pd-Mn/Al_2O_3$ (Pd/Mn = 1.0) > $Pd-Mn/Al_2O_3$ (Pd/Mn = 0.75) > $Pd-Mn/Al_2O_3$ (Pd/Mn = 0.5) > Pd/Al_2O_3. As expected, the selectivity to n-hexane of $Pd-Mn/Al_2O_3$ catalysts is also slightly decreased from Pd/Al_2O_3 catalyst at 1-2 h reaction time as shown in Figure 4.9 because $Pd-Mn/Al_2O_3$ catalyst would increase the hydrogenation to alkenes rather than to alkanes at this a period of time. As reported by Suriyaphaparkorn (2013), the $Pd-Mn/Al_2O_3$ catalysts are more selective than $Pd-Cu/Al_2O_3$ catalysts. In contrast, the $Pd-W/Al_2O_3$ catalysts are similar selectivity with the $Pd-Mn/Al_2O_3$ catalysts.
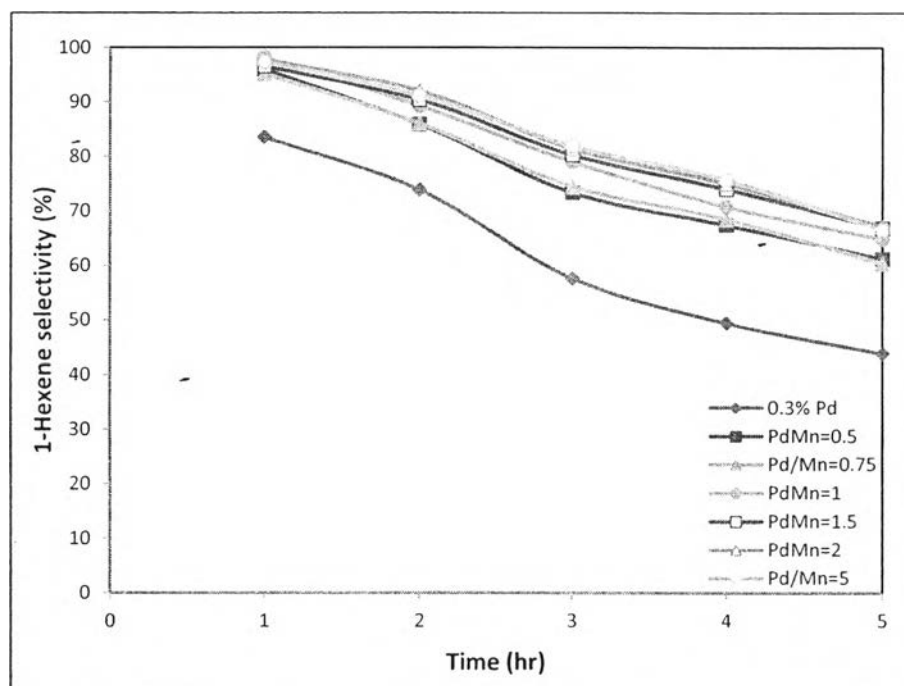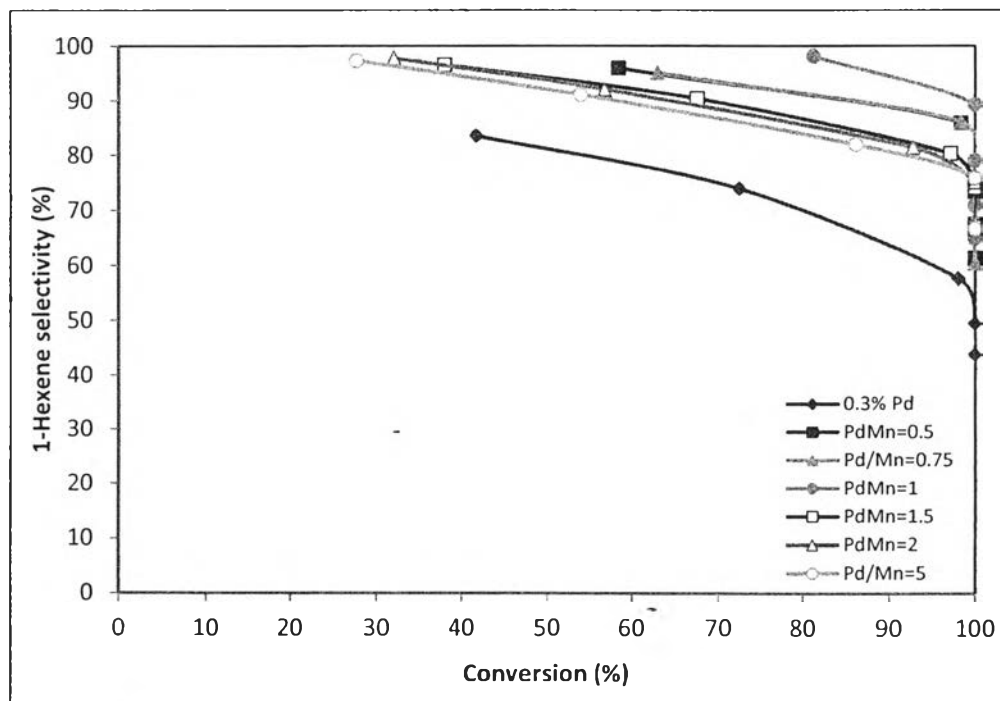

Figure 4.7 1-Hexene selectivity as a function of reaction time for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at various Mn loadings.

Figure 4.8 1-Hexene selectivity for the hydrogenation of 1-hexyne at 40 °C, 1.5 bar, and 1-3 h reaction time over 0.3 wt% Pd/Al₂O₃ at various Mn loadings.
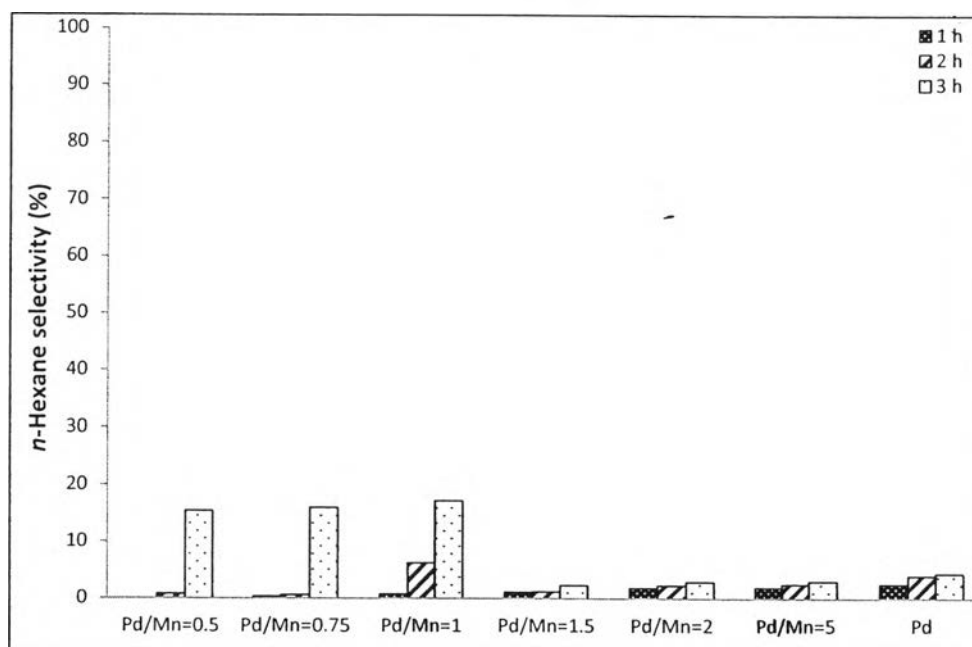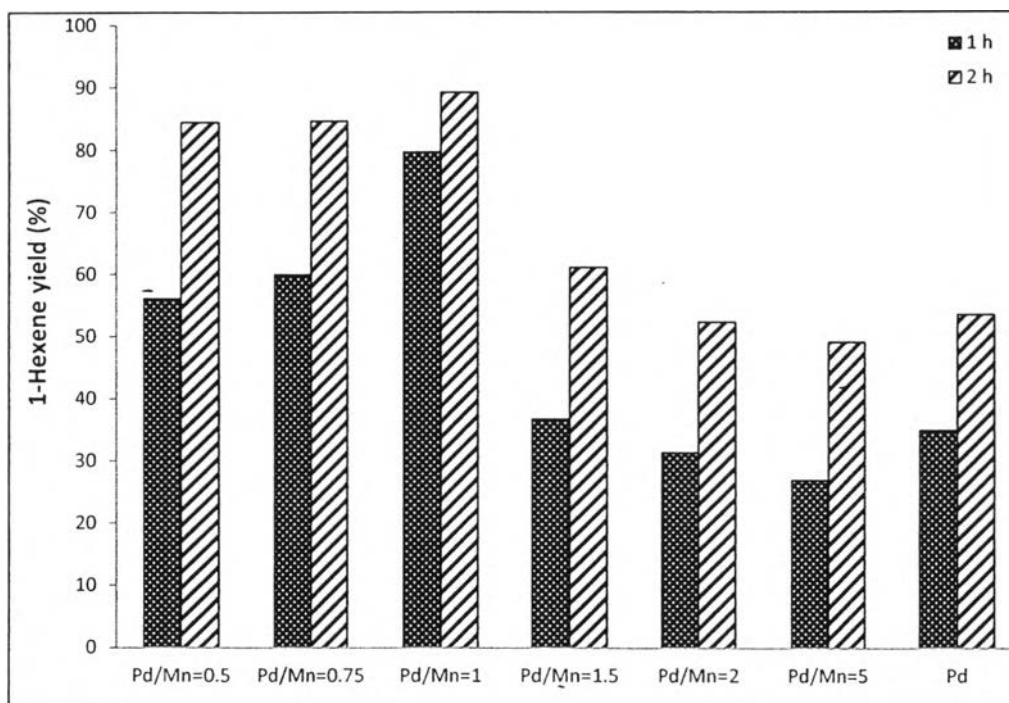

Figure 4.9 *n*-Hexane selectivity for the hydrogenation of 1-hexyne at 40 °C, 1.5 bar and 1-3 h reaction time over 0.3 wt% Pd/Al₂O₃ at various Mn loadings.

Figure 4.10 1-Hexene selectivity as a function of conversion for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al₂O₃ at various Mn loadings.

The 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C, 1.5 bar and 1-2 h reaction time over 0.3 wt% Pd/Al₂O₃ at various Mn loadings is shown in Figure 4.11. The result indicates that the Pd-Mn/Al₂O₃ (Pd/Mn = 0.5, 0.75 and 1.0) catalysts are improved the 1-hexene yield and the Pd-Mn/Al₂O₃ (Pd/Mn = 1.5) catalyst is small increase in 1-hexene yield from the 1-hexene yield of Pd/Al₂O₃ catalyst. Moreover, the 1-hexene yield of the Pd-Mn/Al₂O₃ (Pd/Mn = 0.5, 0.75 and 1.0) catalysts are over 84% at 2 h reaction time. Conversely, the Pd-Mn/Al₂O₃ (Pd/Mn = 2.0 and 5.0) catalysts are slightly decrease in 1-hexene yield from the 1-hexene yield of Pd/Al₂O₃ catalyst. The rank of 1-hexene yield found is: Pd-Mn/Al₂O₃ (Pd/Mn = 1.0) > Pd-Mn/Al₂O₃ (Pd/Mn = 0.75) > Pd-Mn/Al₂O₃ (Pd/Mn = 0.5) > Pd-Mn/Al₂O₃ (Pd/Mn = 1.5) > Pd/Al₂O₃ > Pd-Mn/Al₂O₃ (Pd/Mn = 2.0) > Pd/Al₂O₃ (Pd/Mn = 5.0).
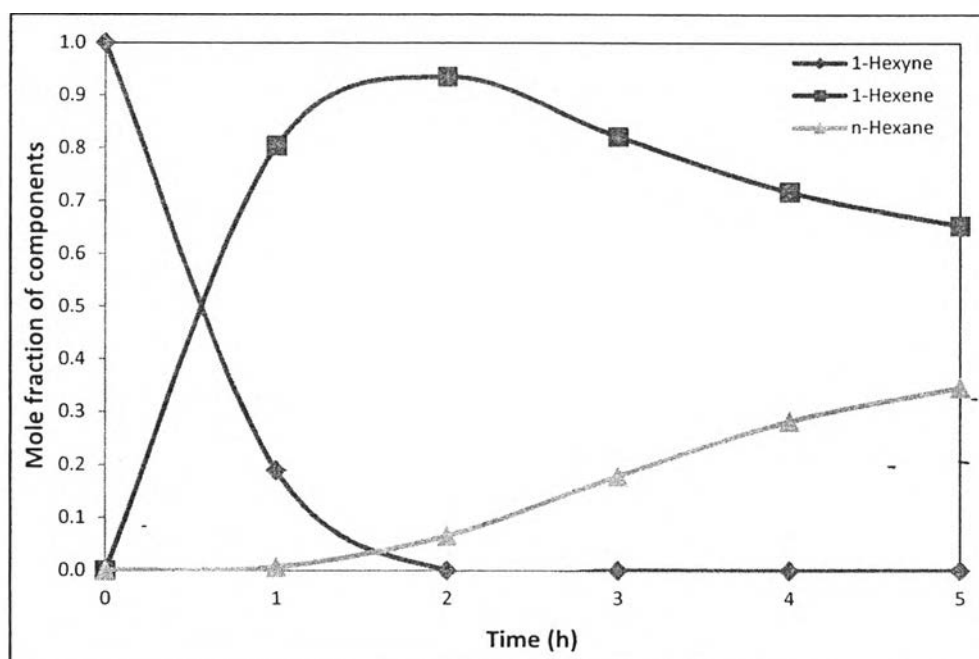
Figure 4.11 1-Hexene yield for the hydrogenation of 1-hexyne at 40 °C, 1.5 bar and 1-2 h reaction time over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings.
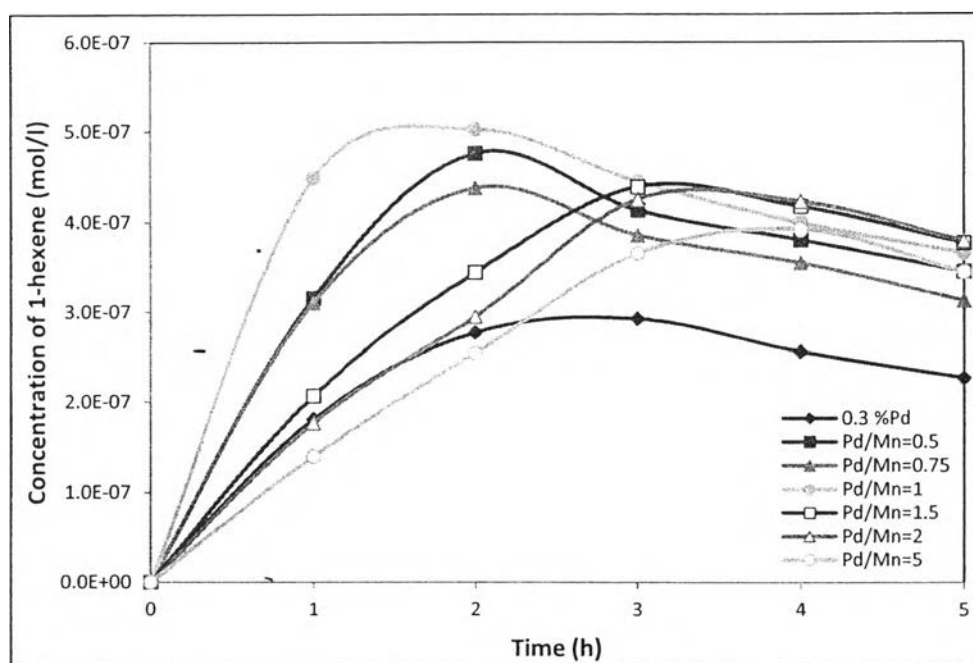
The mole fraction profiles for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1) catalyst is shown in Figure 4.12. It can be seen that 1-hexene is the nearly product of reaction formed until 1-hexyne reaches a high level of conversion. At longer reaction times, 1-hexene reacts to form *n*-hexane and tends to decrease gradually with a continuous reaction. It is suggested that the 1-hexyne is capable to saturate the catalyst surface which displaces the 1-hexene from the catalyst surface and inhibits the readsorption (Alves *et al.*, 2007). Only when the concentration of 1-hexyne is low, can the 1-hexene undergo consecutive reaction (Tew *et al.*, 2011). In other words, the 1-hexene product is adsorbed more weakly than the 1-hexyne and the 1-hexene is more easily desorbed than the 1-hexyne on these catalysts (Kittisakmontree *et al.*, 2013).

The concentration profiles of 1-hexene and *n*-hexane for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings is shown in Figure 4.13 and Figure 4.14, respectively. It can be observed that Pd-

Mn/Al$_2$O$_3$ (Pd/Mn = 0.5, 0.75 and 1.0) catalysts reach the highest point and start to decrease at 2 h reaction time as Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1.0) catalyst has the fastest initial rate of 1-hexyne hydrogenation reaction, but the concentration of 1-hexene will decrease rapidly at longer reaction times because 1-hexene will consecutively react to form n-hexane at a high level of 1-hexyne conversion. The Pd/Al$_2$O$_3$ and Pd-Mn/Al$_2$O$_3$ (Pd/Mn = 1.5, 2.0 and 5.0) catalysts reach the highest point and start to decrease at 3 h reaction time. The 1-hexene concentration of Pd-Mn/Al$_2$O$_3$ catalysts are all higher than Pd/Al$_2$O$_3$ catalyst except for Pd-Mn/Al$_2$O$_3$ catalysts (Pd/Mn = 5.0) at 1-2 h reaction time, it may be a much lower 1-hexyne conversion of Pd-Mn/Al$_2$O$_3$ catalysts (Pd/Mn = 5.0) than the Pd/Al$_2$O$_3$ catalyst. The n-hexane concentration of Pd-Mn/Al$_2$O$_3$ catalysts are all higher at nearly full conversion of 1-hexyne than Pd/Al$_2$O$_3$ catalyst. In contrast, the n-hexane concentration of Pd-Mn/Al$_2$O$_3$ catalysts are all lower at low conversion of 1-hexyne than Pd/Al$_2$O$_3$ catalyst.

Figure 4.12 Mole fraction profiles for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over Pd-Mn/Al$_2$O$_3$ (Pd/Mn =1).

Figure 4.13 Concentration profiles of 1-hexene for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings.
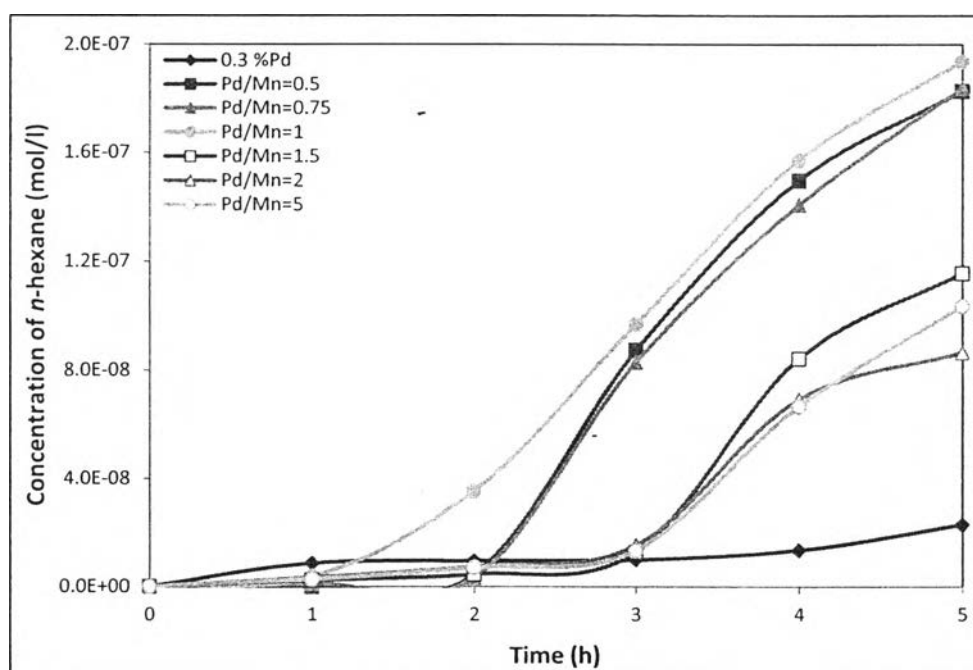
Figure 4.14 Concentration profiles of n-hexane for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al$_2$O$_3$ at various Mn loadings.

The results indicate that the Pd-Mn/Al$_2$O$_3$ catalysts can improve the rate of 1-hexyne hydrogenation reaction and the rate of 1-hexene hydrogenation reaction. Besides, the Pd-Mn/Al$_2$O$_3$ catalysts can also suppress the 1-hexyne hydrogenation to *n*-hexane causes the 1-hexene selectivity is higher than Pd/Al$_2$O$_3$ catalyst.