# CHAPTER IV

# RESULTS AND DISCUSSION

The main topic of this chapter is the effect of regeneration on the properties of Pd-Ag catalysts after $N_2O$ activation. In order to accommodate the detailed consideration, this chapter is categorized into three sections. The characterization of commercial catalysts (both fresh and spent catalysts) used in this study is firstly discussed in section 4.1. Catalyst evaluation for selective hydrogenation of acetylene is described in section 4.2. And section 4.3 is additional characterization of the catalysts in order to postulate the synergetic effect of pretreatment.

## 4.1 Commercial Catalysts Characterization

Commercial catalysts ($Pd\text{-}Ag/Al_2O_3$, Ag : Pd = 6) are fresh and spent catalysts from different positions of the acetylene hydrogenation reactor, so it contained different amounts of carbon deposit. The amount of carbonaceous deposits on the spent catalysts, catalyst structure and metal dispersion are discussed in this section.

### 4.1.1 Catalyst Structure

Phase identification is carried out on the basis of data from X-ray diffraction analysis. The XRD patterns of fresh and spent commercial catalysts are shown in Figure 4.1. All the XRD peaks indicate the presence of alumina in both alpha and transition phases. No XRD peaks for palladium and silver metal or oxides were observed due probably to the very low amount of the metals present on the catalysts and/or overlapping with the alumina peaks. All the XRD peaks of fresh catalysts are similar to those of spent catalysts in terms of both position and shape. It is suggested that the conditions used in selective acetylene hydrogenation in industrial does not affect to phase and crystal size of alumina even the catalyst is used for a long period of time.

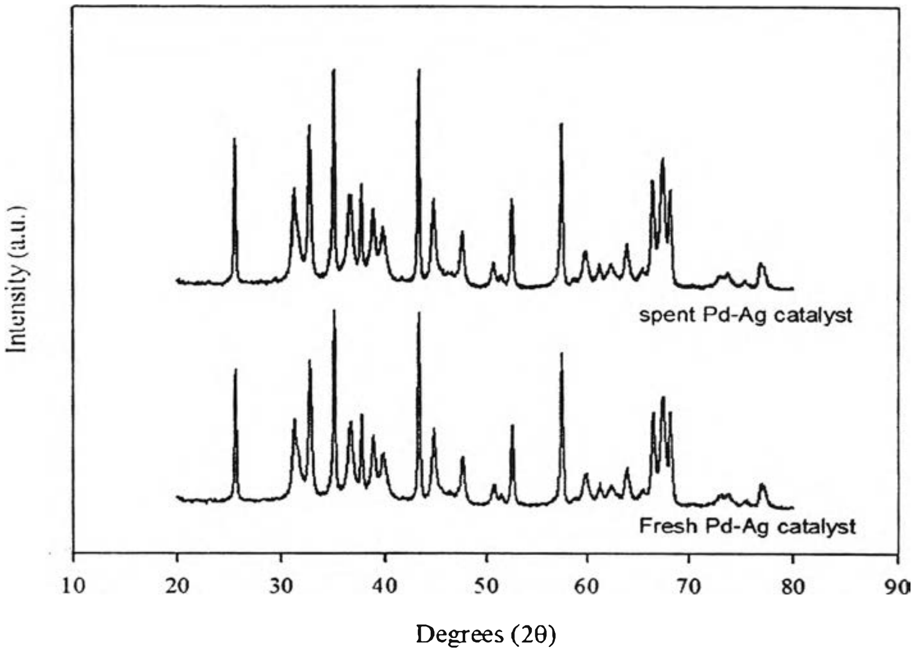


**Figure 4.1** XRD patterns of fresh and spent Pd-Ag/$Al_2O_3$ commercial catalysts.

### 4.1.2 Concentration of Carbon Deposit and Metal Active Sites

The amount of carbonaceous deposits on the spent catalysts was measured by temperature programmed oxidation technique and shown in Figure 4.2. After reaction, coke may deposit on the catalyst surface and cover the active metal resulting in loss of activity [Kim, W. J. *et al.*, 2003]. The amount of carbon deposits was found to be in the order of spent 1 < 2 < 3 < 4. The difference in the amount of carbon deposits on Pd-Ag catalysts may be induced by different reaction conditions such as sample position, sample temperature, etc. However, most of the carbon deposits appeared to be burned off at ca. 500-550°C.

Coke concentration in term of wt% measured by weight loss technique and metal active sites of each samples are summarized in Table 4.1. The results of wt% of carbon deposits are consistent with the results from TPO. As %coke deposits increased the catalyst active sites decreased suggesting that the active surface of Pd were blocked by the carbon deposits.

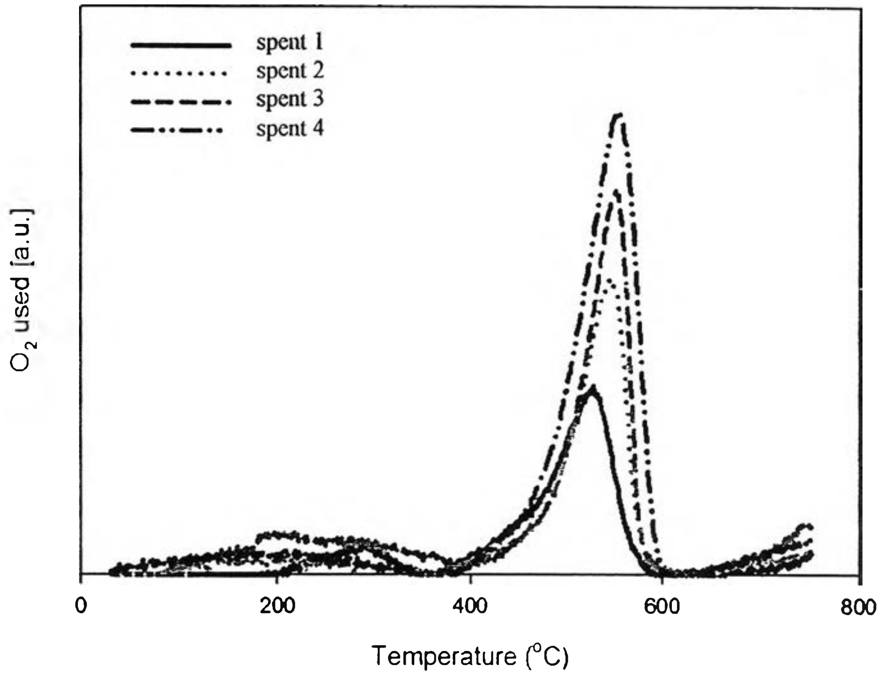


**Figure 4.2** Temperature programmed oxidation (TPO) of the catalysts

**Table 4.1** Coke concentration and active site of fresh and spent catalyst.

| Sample | %coke | Active site ($*10^{-17}$site/g) | |
|---|---|---|---|
| | | untreated | $N_2O$-treated |
| Cat A (Fresh) | 0 | 2.76 | 3.77 |
| Spent 1 | 0.18 | 1.54 | 1.06 |
| Spent 2 | 0.24 | 0.58 | 0.22 |
| Spent 3 | 0.28 | 0.29 | nil |
| Spent 4 | 0.54 | nil | nil |

The catalyst samples with coke deposits (spent 1-4) were then regenerated at 500°C for 2 h using different $O_2$ concentration (1% and 21%$O_2$) and named cat B- E. After regeneration, catalyst active sites were measured again by CO chemisorption technique and results are given in Table 4.2. It was found that the catalyst active sites were recovered for most of the catalyst samples after regeneration with either $O_2$ 1%

or 21% except that of cat E (the highest coke deposits) that regeneration was incomplete when 1%$O_2$ was used resulting in lower amount of active Pd sites.

The regenerated catalyst active sites were measured again by CO chemisorption with and without $N_2O$ pretreatment, the results are shown in Table 4.3. It was found that $N_2O$ pretreatment can increased the active sites only for the fresh Pd-Ag catalysts. The $N_2O$ pretreatment of used catalysts did not result in enhancement of Pd active sites. It is suggested that changes in the catalyst geometry/morphology after regeneration may alter the $N_2O$ pretreatment effect.

**Table 4.2** Active sites of spent catalysts after regenerated in various oxygen concentration.

| Sample | Active site ($*10^{-17}$site/g) | |
|---|---|---|
| | Regenerated in 1% $O_2$ | Regenerated in 21% $O_2$ |
| Cat B | 2.83 | 2.60 |
| Cat C | 2.71 | 2.57 |
| Cat D | 2.56 | 2.81 |
| Cat E | 2.34 | 2.74 |

**Table 4.3** Active sites of catalysts with and without $N_2O$ pretreatment.

| Sample | Active site ($*10^{-17}$site/g) | |
|---|---|---|
| | untreated | $N_2O$-treated |
| Cat A | 2.76 | 3.77 |
| Cat B | 2.60 | 2.62 |
| Cat C | 2.57 | 2.55 |
| Cat D | 2.81 | 2.64 |
| Cat E | 2.74 | 2.58 |

## 4.2 Evaluation of Catalyst Performance

The performance of the catalysts for selective hydrogenation of acetylene is generally evaluated in terms of acetylene conversion and ethylene gain. Acetylene conversion is defined as moles of acetylene consumed with respect to acetylene in feed. Ethylene gain is the ratio of the amount of acetylene converted to ethylene and total amount of acetylene consumed. Ideally, there should be one acetylene molecule converted for every hydrogen molecule consumed, or 100% ethylene gain. In actual practice, some hydrogen will always be consumed in the side reaction of ethylene conversion to ethane. The ethylene gain can be measured by observing the change in the ethane and ethylene from the inlet and outlet. However, this is not practical since ethylene in feed is much more than acetylene, so change of 0.05% in the measurement would be a 10% change in ethylene gain. It is more convenient to calculate ethylene gain by measured hydrogen consumed in the converter and the amount of acetylene converted. The performances of the catalyst in this study were therefore reported in terms of acetylene conversion and ethylene gain observed from hydrogen and acetylene concentrations as detailed below:

Ethylene gain is considered from the following reaction:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad (4.1)$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \qquad (4.2)$$

Ethylene gain is defined as the ratio of those parts of acetylene that are hydrogenated to ethylene to the amount of totally hydrogenated acetylene:

$$C_2H_4 \text{ gain } (\%) = 100 \times \frac{C_2H_2 \text{ hydrogenated to } C_2H_4}{\text{totally hydrogenated } C_2H_2} \qquad (i)$$

where totally hydrogenated acetylene is the difference between moles of acetylene in the product with respect to those in the feed ($dC_2H_2$).

Acetylene hydrogenated to ethylene is the difference between the total hydrogenated acetylene ($dC_2H_2$) and the ethylene being loss by hydrogenation to ethane (equation 4.2). Regarding the difficulty in precise measurement of the ethylene change in the feed and product, the indirect calculation using the difference in the hydrogen amount (hydrogen consumed: $dH_2$) is used.

The ethylene being hydrogenated to ethane is the difference between all the hydrogen consumed and all the acetylene having been totally hydrogenated.

$C_2H_4$ gain from equation (i) can be rewritten as:

$$C_2H_4 \text{ gain } (\%) = \frac{100\times[dC_2H_2 - (dH_2\text{-}dC_2H_2)]}{dC_2H_2} \qquad \text{(ii)}$$

Or in other words, as equations (4.1) and (4.2) show, 2 moles of hydrogen are consumed for the acetylene lost to ethane, but only 1 mole of hydrogen for the acetylene gained as ethylene. The overall gain can also be written as:

$$C_2H_4 \text{ gain } (\%) = 100\times[2 - \frac{dH_2}{dC_2H_2}] \qquad \text{(iii)}$$

Equations (ii) and (iii) are, of course the same, and ethylene gain discussed in this research is then calculated, based on equation (iii). This value is the percentage of the theoretically possible ethylene gain which has been achieved in the operation. A positive value represents net production of ethylene, when the negative value refers to ethylene loss. But due to selectivity of catalyst used in this study is very high, so calculated ethylene gain can be near or even more than 100%. Therefore, ethylene gain is reported in term of normalized ethylene gain.

### 4.2.1 Time on Stream

The performance of the catalysts for selective acetylene hydrogenation was measured as a function of time on stream. According to the temperature dependence result (Appendix F), the suitable temperature range used in comparison of catalytic performance is 60-70°C when acetylene conversion was not close to 100%. Reaction test was performed at 70°C and a GHSV of 5400 $h^{-1}$ for 10 h. Observation of the catalytic behavior was carried out every 1 h as illustrated in Figure 4.3. The conversion and ethylene gain of fresh catalyst started quite high but it seemed to slightly decrease during the first 8 h. This may be resulted from its high activity, so some heavy hydrocarbon was formed on its surface. In the case of regenerated spent-catalyst, their activity and selectivity are constant within a few hours. It is in good agreement with the data from industrial that selectivity of used catalyst is higher than the new ones. For pretreatment effect, in the case of fresh catalyst, pretreatment with $N_2O$ can enhance conversion by 25% and ethylene gain for 15%. But $N_2O$ pretreatment effect on the regenerated spent-catalysts is not significant neither activity nor selectivity. The results suggest that there might be some changes in the catalyst properties after being used in acetylene hydrogenation reaction and regenerated such as Pd-Ag geometry and morphology that resulted in different phenomena observed during $N_2O$ pretreatment and acetylene hydrogenation reaction between fresh and used catalysts.

### 4.2.2 Dependence of Catalytic Performance with Amount of $N_2O$

This section is an attempt to find the effective amount of $N_2O$ to use in pretreatment. It is useful for the industrial which is interested in this method. Due to less pronounced effect of pretreatment on the regenerated catalysts, only fresh catalyst was used in this section. Variation of acetylene conversion and ethylene gain with the amount of $N_2O$ is illustrated in Figure 4.4

The acetylene conversion and ethylene gain using low amount of $N_2O$ pretreatment were both high compared to the use of higher amount of $N_2O$. The effective amount of $N_2O$ was found to be between 50-100 μl/g of catalyst.

### 4.2.3 Dependence of Catalytic Performance with Pretreatment Temperature

Another crucial parameter for pretreatment is temperature at which $N_2O$ is introduced to the catalyst after reduction. Figure 4.5 depicts the effect of pretreatment temperature on acetylene conversion and ethylene gain over Pd-Ag/$Al_2O_3$ commercial catalysts. The amount of $N_2O$ is kept constant at 100 μl/g. Pretreatment at 100°C seems to result in the optimum catalyst performance.

From the reactivity results, it can be concluded that the only fresh Pd-Ag/$Al_2O_3$ can be activated for the selective hydrogenation of acetylene by pretreatment with $N_2O$. The effect of pretreatment on regenerated catalysts in term of both activity and selectivity are less pronounced. However, the regenerated catalysts show higher stability for 10 h time on stream so higher ethylene gain can be expected. How the regeneration affect the result of pretreatment with $N_2O$ is described in the following sections.

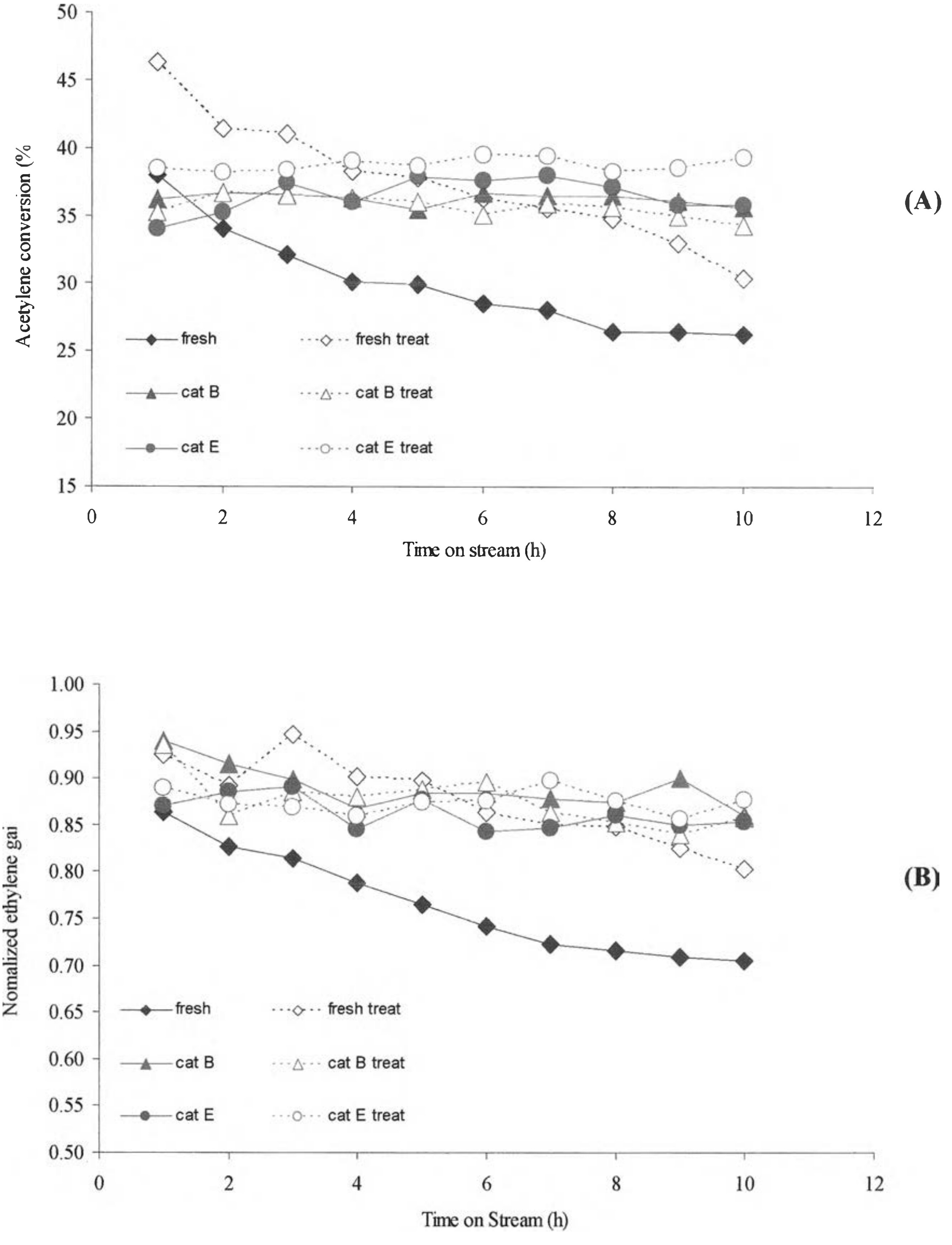
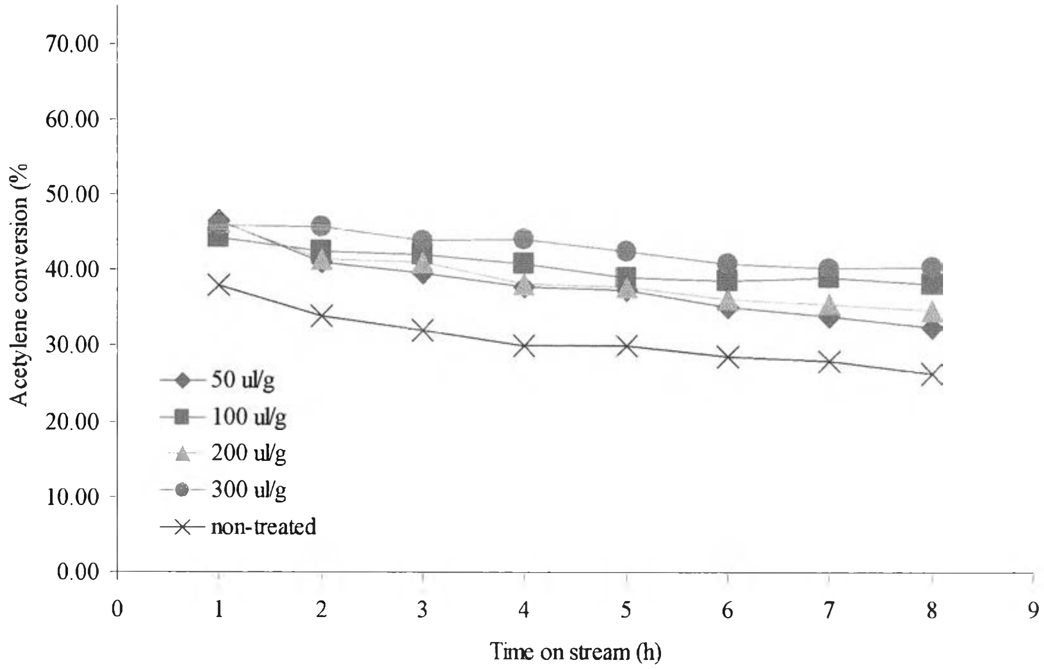
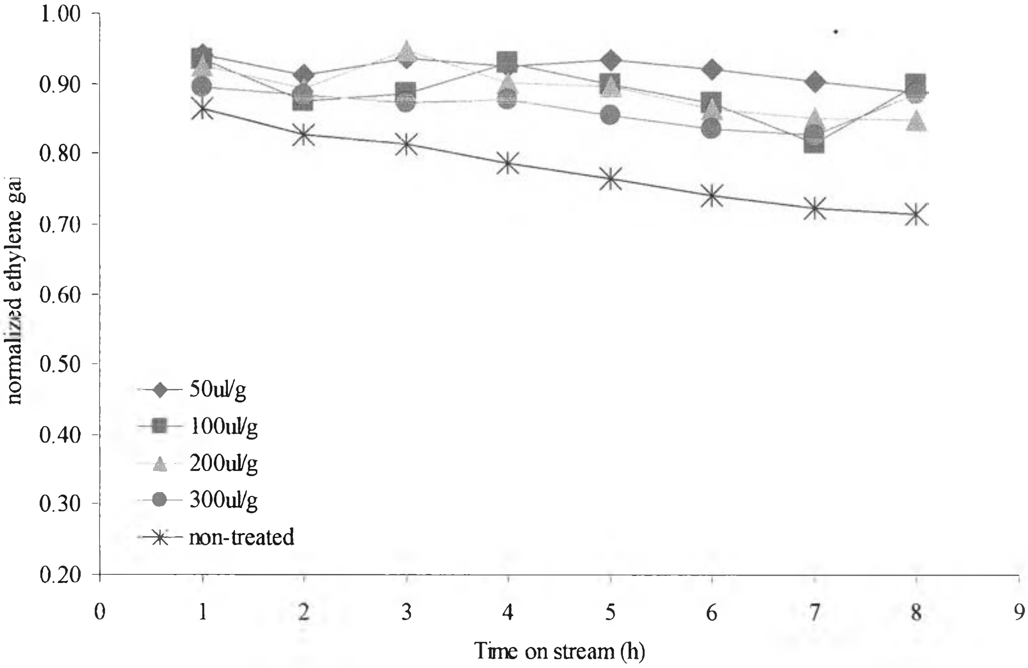


**Figure 4.3** Dependence of the catalytic performance of commercial catalyst as a function of time on stream: (A) % acetylene conversion and (B) normalized ethylene gain Pretreatment temperature, 90°C; reaction temperature, 70°C; GHSV, 5400 h$^{-1}$.



**(A)**



**(B)**

**Figure 4.4** Effect of amount of $N_2O$ on catalyst performance as function of time on stream: (A) % acetylene conversion and (B) normalized ethylene gain. Pretreatment temperature, 90°C; reaction temperature, 70°C; GHSV, 5400 $h^{-1}$.

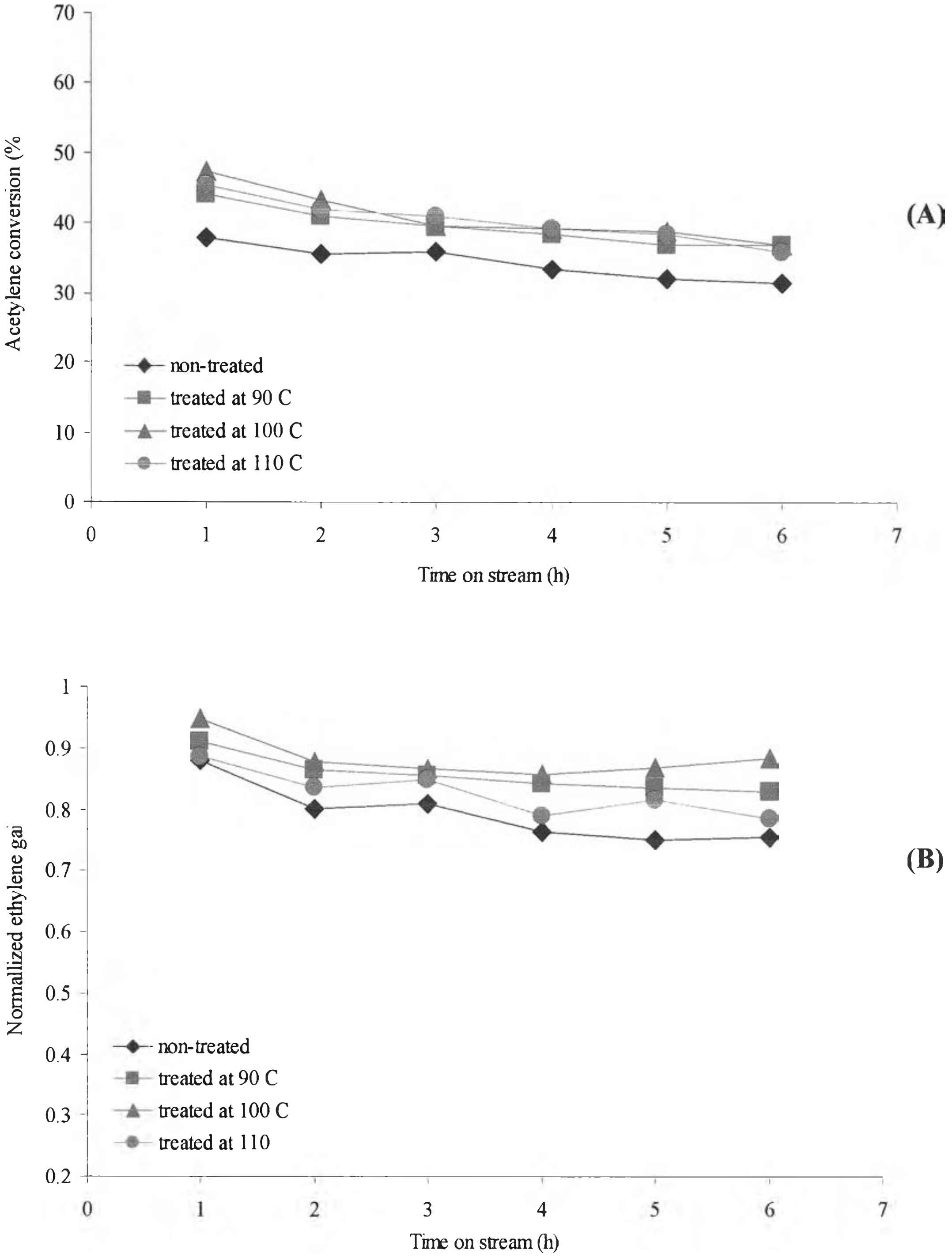


**Figure 4.5** Effect of pretreatment temperature on catalyst performance as function of time on stream: (A) % acetylene conversion and (B) normalized ethylene gain. Amount of $N_2O$, 100 μl/g; reaction temperature, 70°C; GHSV, 5400 $h^{-1}$.

## 4.3 Additional Catalysts Characterization

According to difficulties in characterization of very low metal loading commercial catalysts, the characterization here was performed on the 1wt%Pd-3%Ag/$Al_2O_3$ catalysts. The catalyst structure and metal dispersion are firstly discussed. Surface composition and electronic state of metal surface are also investigated. Finally, study on surface species formation is focused.

### 4.3.1 Catalyst Structure and Morphology

It is well known that the catalyst structure and morphology have crucial effects on catalyst properties. Their performances are strictly related to the preparation procedure and to the nature of the support which both determine the critical parameter represented by the metal particle size [Sárkány Á., *et al.*, 2002]. Studies on the effect of particle size for Pd/$Al_2O_3$ catalysts suggested that increase in metal dispersion decreased the specific activity of small particle catalyst [Asplund, S., *et al.*, 1995, Hub, S., *et al.*, 1988, Boitiaux, J.P., *et al.*, 1983, Gigola, C.E., *et al.*, 1986], while small particles of a medium dispersed catalyst exhibited slightly higher activity [Sárkány, Á., *et al.*, 1986]. Bulk composition and phase transitions of the catalyst, especially for a bimetallic system, are of another importance to be considered. Investigation of the catalyst structure and morphology by specific surface area measurements (BET), and XRD is performed and detailed as follows:

#### 4.3.1.1 Specific Surface Area

Table 4.4 shows the BET surface area of commercial catalysts and supported alumina Pd, Ag and Pd-Ag sample both sequent and co-impregnation. Alumina from commercial catalysts has surface area of 18.4 $m^2/g$, whereas surface area of alumina used for impregnation is 15.5 $m^2/g$. For commercial catalysts, which have very low metal loading, introduction of Pd and Ag onto the alumina support does not affect the surface area of the support. But in the case of 1wt%Pd-3wt%Ag/$Al_2O_3$ impregnation of Pd and Ag slightly decreased the surface area of alumina. However, when the

$Pd/Al_2O_3$ sample is re-impregnated with Ag, the surface area was not further decreased. The difference in surface area of $Pd\text{-}Ag/Al_2O_3$ prepared from different method, sequent and co-impregnation, is insignificant. Pretreatment with $N_2O$ was not affect the surface area of alumina-supported Pd-Ag catalyst [B. Ngamsom, 2002].

**Table 4.4** Surface areas of commercial catalyst, alumina supported Pd, Ag, and Pd- Ag catalysts.

| Sample | BET surface area ($m^2/g$) |
|---|---|
| $Al_2O_3$ from commercial catalysts | 18.4 |
| Commercial catalyst | 18.0 |
| $Al_2O_3$ | 15.5 |
| $Pd/Al_2O_3$ | 14.1 |
| $Pd\text{-}Ag/Al_2O_3$ (sequent-impregnation) | 13.9 |
| $Pd\text{-}Ag/Al_2O_3$ (co-impregnation) | 13.7 |

#### 4.3.1.2 Catalyst Structure and Crystallite Size

The phase identification is carried out on the basis of data from X-ray diffraction analysis. XRD diffractograms of the alumina supported 1wt%Pd-3wt%Ag catalysts as well as reference spectra of monometallic Pd and Ag are depicted in Figure 4.6. Apart from alumina peaks, the calcined Pd sample exhibit oxide form of Pd; PdO (101) at $2\theta = 33.9^\circ$. The reduced Pd sample shows main peaks of Pd (111) ($2\theta = 40.0^\circ$) and Pd (200) ($2\theta = 46.7^\circ$). The calcined and reduced Ag samples show main peaks of Ag at $2\theta = 38.1^\circ$, $44.3^\circ$ and $64.4^\circ$, respectively without any peaks corresponding to $Ag_2O$ ($Ag_2O(111) = 32.85$, $Ag_2O(220)=55.01$). The calcined Pd-Ag sample also exhibits oxide form of Pd; PdO (101) and PdO (311). And peaks corresponding to $Ag_2O$ were also not seen, except for Pd-Ag (co-impreg.) and regenerated Pd-Ag (sequent-impreg.) which were calcined at 500°C in preparation step and regeneration step. After reduction, the position shift of the Pd features towards the lower degrees (-0.4-0.6) for (111) plane indicates that solid solution

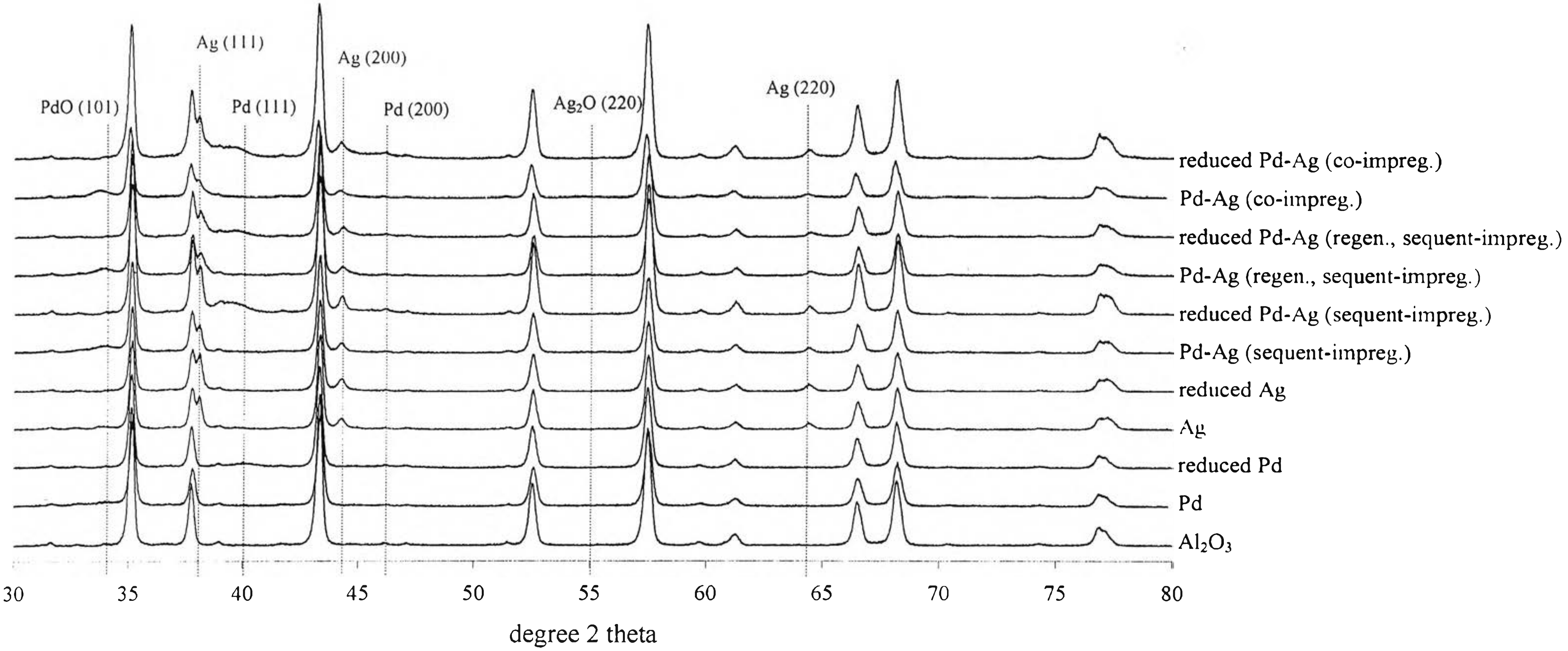


**Figure 4.6** XRD profiles of the alumina support and alumina-supported Pd, Ag and Pd-Ag catalysts.

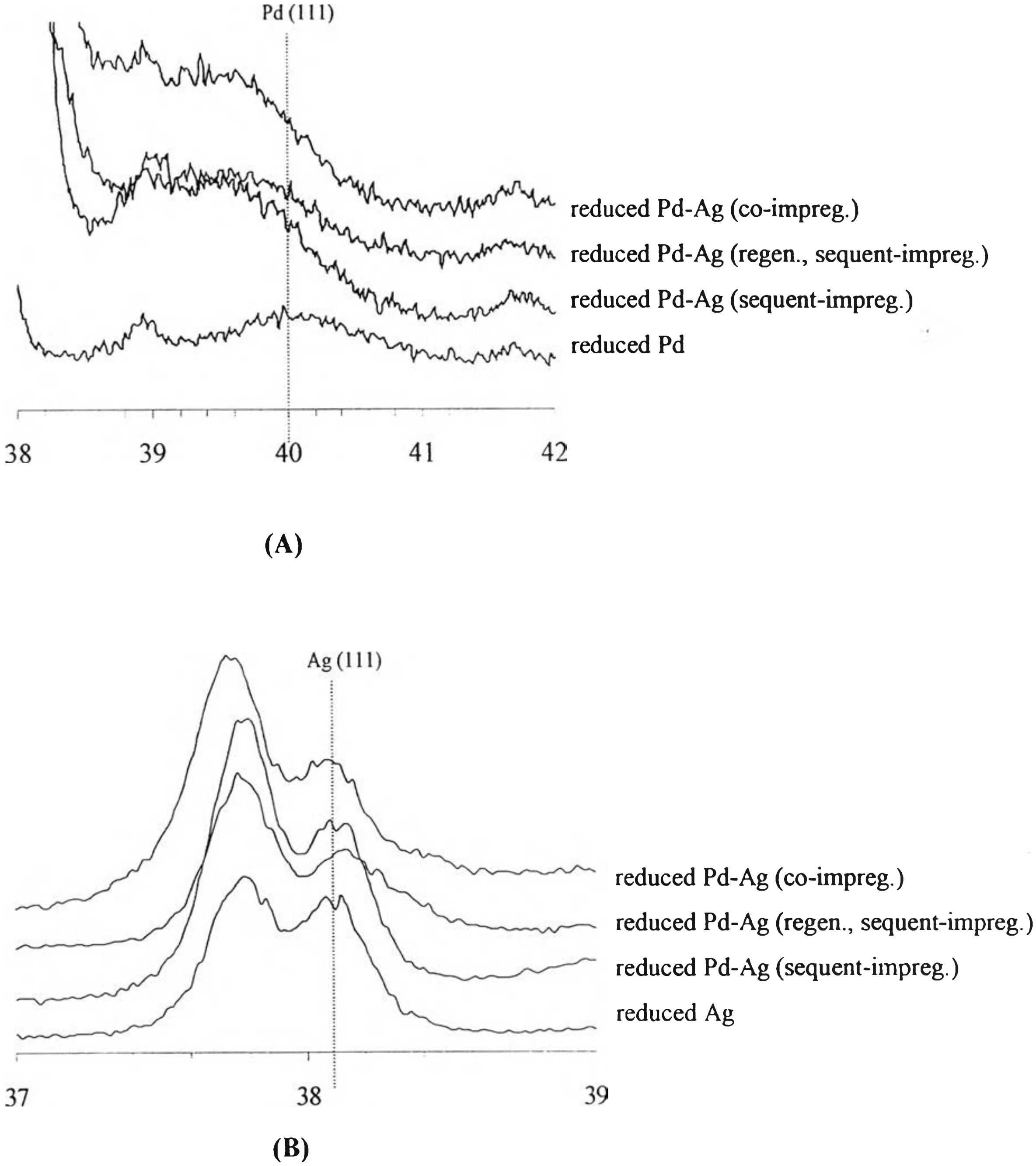


**Figure 4.7** **(A)** and **(B)** are magnified details of the Pd (111) and Ag (111), respectively.

between Pd and Ag was partly formed after reduction. However, Ag particles still exist in the bulk and possibly segregate on the Pd-Ag solid solution as the lower surface energy of Ag compared to that of Pd [111]. The results observed from XRD are in good agreement with the XPS results where alloy formation between Pd-Ag is suggested from the significantly negative shift of Pd $3d_{5/2}$ binding energy as will be discussed in the following section. And pretreatment with $N_2O$ unaltered the peak positions compared to the untreated (reduced) Pd-Ag sample [B. Ngamsom, 2002]. Accordingly, there is no change in the bulk composition of the catalyst upon pretreatment.

Table 4.5 summarized the crystal size of Pd and Ag calculated from their main peaks, Pd (111), Ag (111), according to the Scherrer's method. The difference in Pd particles size of every sample is insignificant. But in the case of Ag, calcinations at 500°C (co-impreg. and regenerated samples) made Ag particles size smaller. The surface of Pd-Ag sample prepared by sequent-impregnation method is in the form of "Pd island" in the "Ag ocean", consequently, the particles size of Ag is large. But in method of co-impregnation Pd and Ag particles would distribute in high dispersion therefore, size of Ag is small. Since the Tamman temperature (defined as half of the bulk melting point in absolute temperature, 480°C for Ag and 650°C for Pd) of Ag are below the temperature in regeneration step (500°C), Ag atom can be mobilized and rearranged with Pd and wide spread on the surface. This may be the reason why the Ag particles is smaller after regenerated.

**Table 4.5** Peak position and crystallite size of alumina supported Pd, Ag and Pd-Ag catalysts from XRD.

| Sample | Peak position (degree 2 theta) | | Crystal size (nm) | |
|---|---|---|---|---|
| | Pd (111) | Ag (111) | Pd | Ag |
| Pd | 40 | - | 6.88 | - |
| Ag | - | 38.1 | - | 80.26 |
| Pd-Ag (sequence-impregnation) | 39.4 | 38.1 | 6.19 | 48.03 |
| Pd-Ag (regenerated, sequence-impregnation) | 39.6 | 38.1 | 7.18 | 26.07 |
| Pd-Ag (co-impregnation) | 39.4 | 38.1 | 6.13 | 27.83 |

### 4.3.2 Metal Active Sites

The Metal active sites of the treated catalysts are shown in Table 4.6. The results are in good agreement to the characterization and catalyst evaluation on commercial catalysts. The active sites of Pd sample are much more than the Pd-Ag bimetallic catalysts, although Pd particle size is the same. Therefore most of Pd particles are covered by Ag. It has been reported in the literature that CO does not chemisorb either on the alumina support or on the Ag particles in supported Pd-Ag bimetallic catalysts [Soma-Noto, Y. *et al.*, 1974., Cormack, D., *et al.*, 1975], but adsorption of CO on Ag at 40°C is also reported [Zhenping Qu, *et al.*, 2004]. Number of metal active sites of regenerated sample is equally to the fresh sample, suggesting that sintering of Pd did not occur and consistent with the XRD results. Only Pd-Ag samples prepared from sequent-impregnation show an increase in the number of palladium active sites. Consequently the arrangement of Pd and Ag on catalyst surface would be the crucial factor of the ineffective pretreatment with $N_2O$ on the regenerated catalysts.

Since every sample but the Pd-Ag (sequent-impreg.) was not affected by pretreatment with $N_2O$, it can be concluded that the catalyst which can be activated by this technique should have surface properties i.e., Pd and Ag arrangement like the sample prepared from sequent-impregnation.

**Table 4.6** Active sites of alumina supported Pd, Ag and Pd-Ag catalysts with and without $N_2O$

| Sample | Active site (*$10^{-18}$site/g) | |
|---|---|---|
| | untreated | $N_2O$-treated |
| Fresh sim. Cat.<br>(sequent-impregnation) | 1.66 | 1.94 |
| Pd-Ag<br>(regenerated, sequent-impregnation) | 1.57 | 1.59 |
| Fresh sim. Cat.<br>(co-impregnation) | 1.35 | 1.39 |
| Pd | 11.8 | 6.46 |
| Ag | 0.65 | 0.18 |
| $Al_2O_3$ | nil | nil |

### 4.3.3 Temperature Programmed Study of Ethylene

Temperature programmed technique was performed in order to obtain an information about ethylene adsorption behavior on the catalyst samples. This study was carried out at 35-800°C after the samples were reduced in $H_2$ at 200°C, and purged with He at the same adsorption temperature. The study was performed for the $Al_2O_3$ support and supported Pd-Ag catalyst with and without pretreatment. All the temperature programmed study profiles are shown in Figure 4.8.

It was found that every sample exhibited two main peaks at ca. 445-480°C and 600-630°C, except for treated Pd-Ag (sequen.-impreg.) that has additional peak at ca.550°C. The peak area of Pd-Ag samples prepared from sequent-impregnation was much more than other sample, it indicates that the amount of ethylene adsorbed on the surface is high. This would be the reason for lower ethylene selectivity found in this sample. The higher in selectivity of this sample when pretreatment was performed has origin from the additional peak at ca. 550°C. This suggests that there is a new site on surface after pretreatment. Therefore some of ethylene molecules were adsorbed on this site (weaker adsorption) instead of another stronger adsorption site (high temperature peak at ca. 630°C) and resulted in higher ethylene gain.

In the case of regenerated catalyst, there is a shift of position for both two peaks from the sequence impregnation sample. The desorption peaks shifted from 460°C to 480°C, resulting in lower ethylene gain, and from 630°C to 606°C, resulting in higher in ethylene gain. Overall, this sample still had high selectivity. After $N_2O$ pretreatment, the desorption peak was slightly shift from 606°C to 596°C; this is consistent with the results from catalyst evaluation that pretreatment with $N_2O$ has insignificant effect on ethylene gain.

For the catalyst prepared by co-impregnation, the pretreatment effect resulted in a shift of both peaks to lower temperature. The desorption peaks at ca. 461°C were shifted to 445°C and peak at ca. 630°C was shifted to 600°C. It indicates that after pretreatment the adsorbed ethylene were easier to desorb resulting in higher ethylene selectivity. To prove this effect, catalytic properties of the Pd-Ag sample (co-impreg.) were tested in selective hydrogenation of acetylene as a function of time on stream for

6 h (not shown here). The result is in good agreement with the ethylene temperature programmed study. The pretreatment with $N_2O$ on such catalyst can enhance the ethylene gain for ca. 4% but an increase in acetylene conversion was also not observed.

It can be concluded that after regeneration there are changes in Pd and Ag metal arrangement on the catalyst surface and result in a decrease of ethylene adsorption site. Changing of surface arrangement is not exactly the same as that of Pd-Ag sample prepared from co-impregnation method since behavior of ethylene desorbed after pretreatment is difference. Pretreatment on Pd-Ag (sequent-impreg.) create a new site of ethylene adsorb and would be the origin of enhancement in ethylene gain. Pretreatment has no effect on the regenerated catalyst in term of ethylene adsorb-desorb behavior. And increase in selectivity of Pd-Ag catalyst (co-impreg.) would be the result from shift of ethylene desorption peaks to lower temperature after pretreatment with $N_2O$.

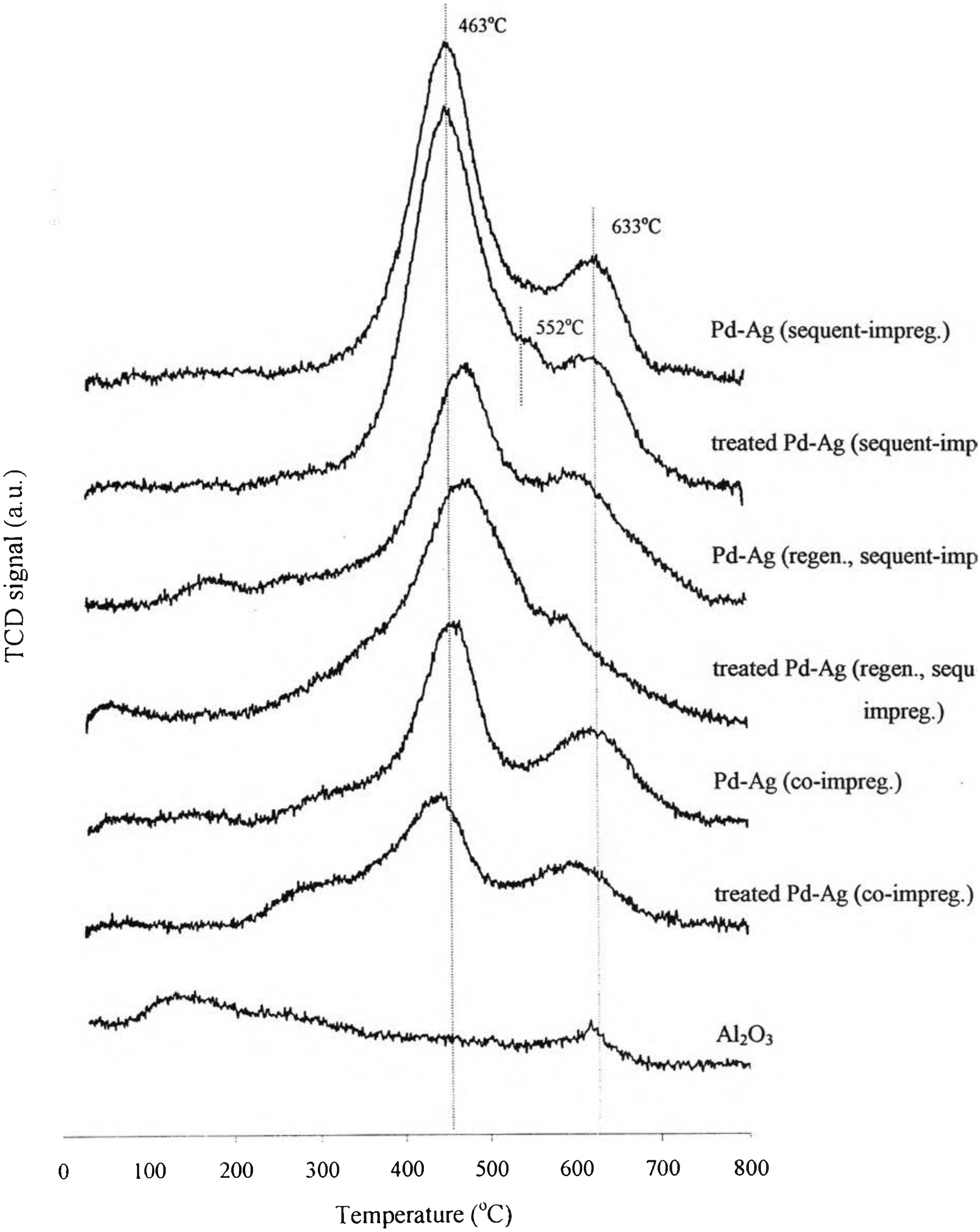


**Figure 4.8** Temperature programmed study profile of alumina supported Pd-Ag catalysts.

### 4.3.4 Surface Composition and Electronic State of Metals

Regarding the results obtained previously, it is found that Ag modified Pd surface and solid solution between Pd and Ag occurred. However, surface concentration of each element has not be elucidated. This section is therefore aimed to study the surface composition as well as the electronic state of the metal catalyst with and without pretreatment using X-ray photoelectron spectroscopy (XPS).

Figure 4.9 illustrates XPS survey spectra for Pd-Ag/$Al_2O_3$ prepared from sequence-impregnation samples. Only the core levels of metallic palladium (Pd 3p and Pd 3d) and its Auger electron signal (Pd (MNN)) are observed but only the most intense core-level peaks (3d for Pd and Ag). Figure 4.10 **(A)** shows X-ray photoelectron spectra of Pd 3d region and **(B)** shows X-ray photoelectron spectra of Ag 3d. Results of XPS study on every sample are summarized in Table 4.7. It is seen that Ag related binding energy for the alumina supported monometallic catalyst are slightly higher than the reference Ag metal bulk value (+0.8 eV). And line broadening (+1.0 eV) occurs compared to that observed from bulk Ag, corresponding to charging from alumina. The Ag $3d_{5/2}$ binding energies of the Ag and Pd-Ag/$Al_2O_3$ catalysts line in the range 370.9-371.4 eV, indicating metal form of Ag. The Pd $3d_{5/2}$ binding energies of Pd-Ag catalysts are found to be 337.9-338.9 eV, which were higher than that observed on the Pd/$Al_2O_3$ sample (binding energy of Pd $3d_{5/2}$ is 337.4 eV). It is suggested that there was a change of electronic state of Pd in Pd-Ag/$Al_2O_3$ catalysts. Pd-Ag alloy or solid solution can be formed by electron density transfer from Ag to Pd resulting in the appearance of negative charge on Pd and positive charge on Ag.

The Pd $3d_{5/2}$ binding energy obtained from the fresh Pd-Ag sample was unaltered with respect to that of the fresh monometallic Pd sample (BE=339.9 eV), indicating PdO on the surface. After reduction, the core level Pd $3d_{5/2}$ electron shifted to 338.5 eV (+1.1 eV from the monometallic Pd (BE=337.4 eV)). It is also observed a +0.1 eV shift of the Ag $3d_{5/2}$ binding energy for the reduced Pd-Ag sample (BE =371 eV), with respect to the reduced monometallic Ag sample (BE=370.9 eV).

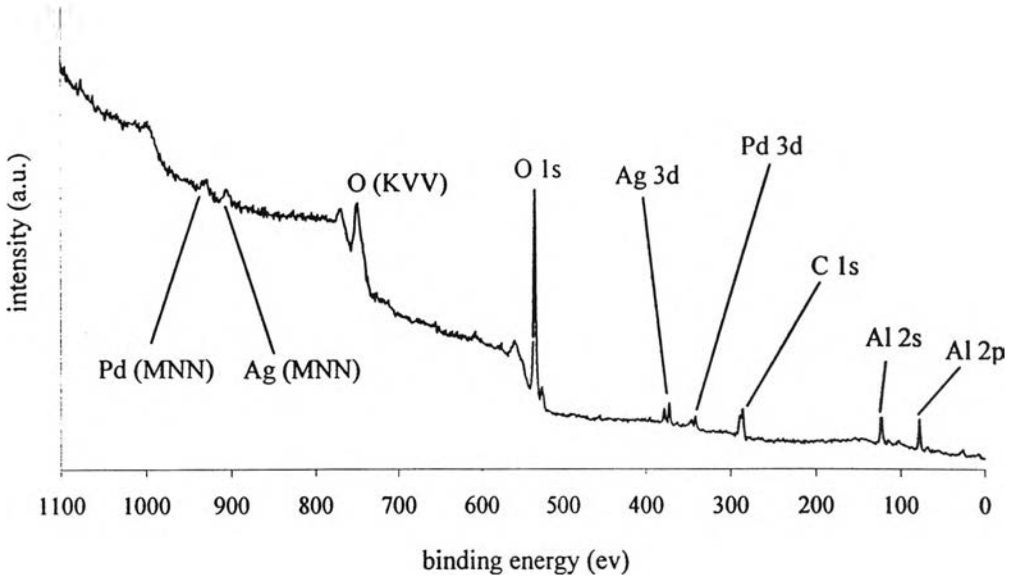


**Figure 4.9** XPS survey spectra for supported Pd-Ag catalysts

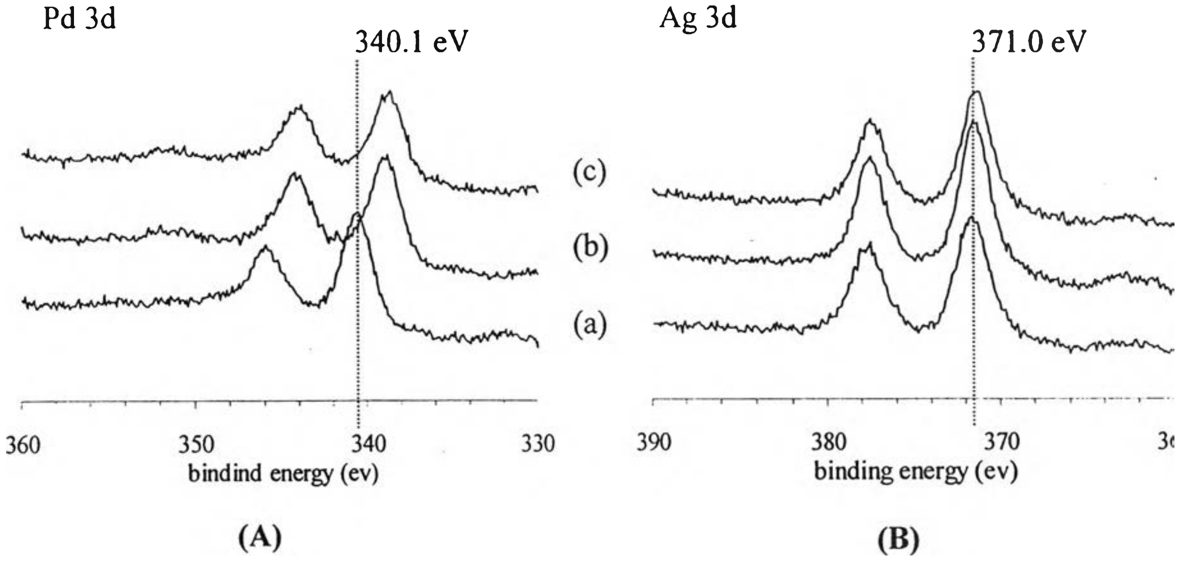


**Figure 4.10** XPS Pd 3d spectra **(A)** and Ag 3d spectra **(B)** for alumina-supported samples prepared from sequent-impregnation method: (a) was fresh Pd-Ag sample, (b) was reduced Pd-Ag sample, and (c) was $N_2O$ treated sample.

**Table 4.7** XPS binding energies of Ag 3d and Pd 3d species of Pd-Ag/$Al_2O_3$ simulated catalysts before and after regeneration.

| Sample | Pd $3d_{5/2}$ | Ag $3d_{5/2}$ | | Pd:Ag Atomic concentration (%) |
|---|---|---|---|---|
| | Peak position (ev) | Peak position (ev) | FWHM (ev) | |
| Ag metal | - | 370.2 | 1.19 | - |
| Pd | 339.9 | - | - | - |
| Reduced Pd | 337.4 | - | - | - |
| Ag | - | 371.0 | 2.21 | - |
| Reduced Ag | - | 370.9 | 2.18 | - |
| Fresh Pd-Ag | 340.1 | 371.0 | 2.23 | 0.92 |
| | *340.0* | *371.0* | *2.24* | *0.95* |
| | **339.9** | **371.2** | **2.21** | **0.73** |
| Reduced Pd-Ag | 338.5 | 371.0 | 2.07 | 0.73 |
| | *338.4* | *371.0* | *2.07* | *0.65* |
| | **338.9** | **371.4** | **2.01** | **0.58** |
| $N_2O$-treated Pd-Ag | 338.1 | 370.7 | 2.11 | 0.73 |
| | *337.9* | *370.5* | *2.02* | *0.72* |
| | **338.3** | **371.2** | **2.01** | **0.53** |

*Italic numbers represent the values after regeneration.*

**Bold numbers represent the values of co-impregnation.**

After being subjected to $N_2O$ pretreatment, the binding energies measured for Ag $3d_{5/2}$ from most samples show a negative shift in the range of 0.2 to 0.5 eV (from 371.0-371.4 to 370.5-371.2 eV). Modification of Ag in Pd-Ag alloy surface by $N_2O$ treatment, therefore, may occur. The result for Pd-Ag/$\gamma$-$Al_2O_3$ show an increasing Pd surface concentration in Pd-Ag alloy (from Pd:Ag = 1.1 to Pd:Ag = 5.1) this also resulted in a +0.6 eV shift of Pd $3d_{5/2}$ whereas only -0.1eV shift was found on Ag$3d_{5/2}$ [Sales, E.A., *et al.*, 1998]. Thus, the significant shift resulted from $N_2O$ pretreatment in this study should not originated from the change in composition of the Pd-Ag alloy.

The lower palladium fraction at the surface of the reduced sample indicates surface enrichment with silver after reduction (untreated sample). This can be explained by the lower surface energy of Ag (930 erg/cm$^2$) respective to that of Pd (1500 erg/cm$^2$) [Boyer, H.E. in Gell, *et al.*, 1985]. The palladium fraction was not changed when pretreatment was conducted, except those for the regenerated catalyst that palladium fraction increased after pretreated. This is inconsistent to the results from metal active sites measurement and catalyst evaluation.

Based on surface analysis by XPS, it can be concluded that the surface of Pd-Ag/$Al_2O_3$ catalyst after reduction contained solid solution between Pd and Ag with Ag enrichment. Pretreatment with $N_2O$ did not result in an increase amount of palladium on the surface. However, a significant negative shift of the Ag $3d_{5/2}$ on every sample due to pretreatment with $N_2O$ suggests surface modification by $N_2O$.