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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

The calculation shown below is for 1%Pd-3%Ag/Al_2O_3. The alumina support weight used for all preparation is 2 g.

Reagent: - Palladium (II) nitrate hexahydrate ($Pd(NO_3)_2 \cdot 6H_2O$)
Molecular weight = 338.41
- Silver (III) nitrate ($Ag(NO_3)$)
Molecular weight = 169.87
- Support:- Alumina

Calculation for Palladium Impregnation

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Palladium = 1 g
Silver = 3 g
Alumina = 100–(1+3) = 97 g

For 2 g of alumina

Palladium required = 2×1/97 g = 0.0206 g

$$Pd(NO_3)_2 \cdot 6H_2O \text{ required} = \frac{\text{Palladium required} \times \text{MW of } Pd(NO_3)_2 \cdot 6H_2O}{\text{MW of Pd}}$$

$$= 0.0206 \times 338.41/106.42 = 0.0655 \text{ g}$$

Since the pore volume of the alumina support is 0.25 ml/g and the total volume of impregnation solution which must be used is 0.5 ml by the requirement of dry impregnation method, the de-ionised water is added until the total volume of impregnation solution is 0.5 ml.

Calculation for Silver Impregnation

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Palladium = 1 g

Silver = 3 g

Alumina = 100−(1+3) = 97 g

For 2 g of alumina

Silver required = 2×3/97 g = 0.0618 g

$$\text{Ag(NO}_3\text{) required} = \frac{\text{Silver required} \times \text{MW of Ag(NO}_3\text{)}}{\text{MW of Ag}}$$

$$= 0.0619\times169.87/107.87 = 0.0975 \text{ g}$$

Since the pore volume of the alumina support is 0.25 ml/g and the total volume of impregnation solution which must be used is 0.5 ml by the requirement of dry impregnation method, the de-ionised water is added until the total volume of impregnation solution is 0.5 ml.

APPENDIX B

CALCULATION CURVES

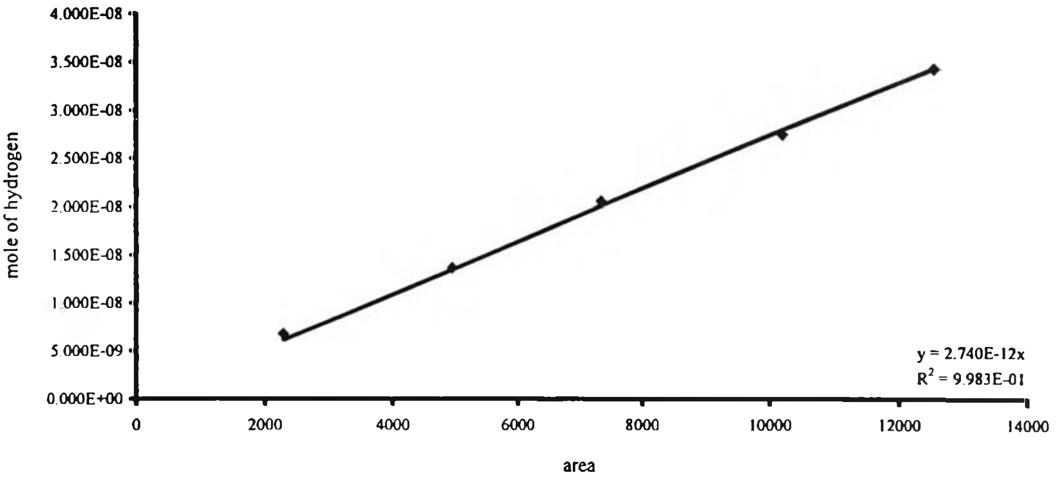

Figure B.1 The calibration curve of hydrogen from TCD of GC-8A.

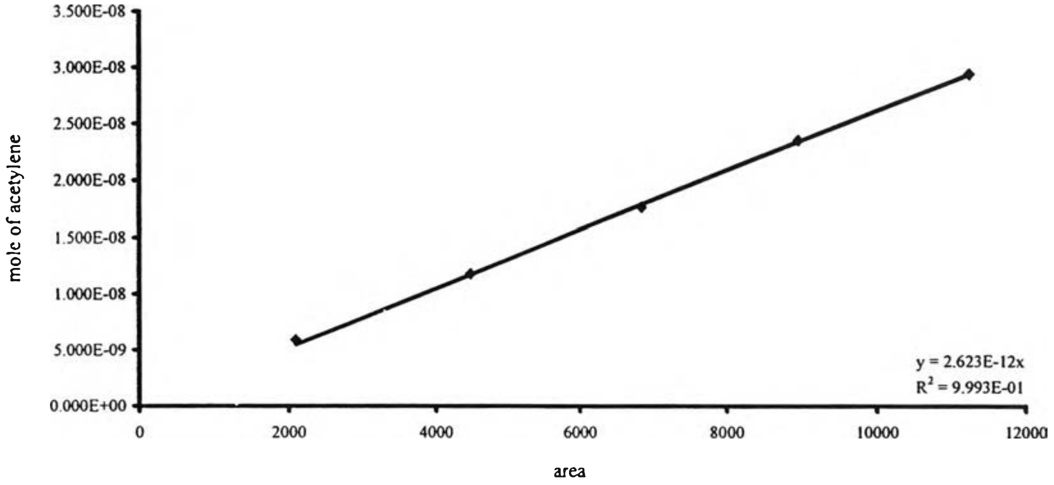

Figure B.2 The calibration curve of acetylene from FID of GC-8A.

APPENDIX C

CALCULATION OF C_2H_2 CONVERSION AND C_2H_4 GAIN

The catalyst performance for the selective hydrogenation of acetylene was evaluated in terms of activity for acetylene conversion and ethylene gain based on the following equations:

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \qquad (C.1)$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \qquad (C.2)$$

Activity of the catalyst for acetylene conversion is defined as moles of acetylene converted with respect to acetylene in the feed:

$$C_2H_2 \text{ conversion (\%)} = \frac{100\times[\text{ mole of } C_2H_2 \text{in feed} - \text{mole of } C_2H_2 \text{ in product}]}{\text{mole of } C_2H_2 \text{in feed}} \qquad (i)$$

where mole of C_2H_2 can be measured employing the calibration curve of C_2H_2 in Figure B.1, Appendix B., i.e.,

mole of C_2H_2 = (area of C_2H_2 peak from integrator plot on GC-8A) × 2.623×10^{-12} (ii).

Ethylene gain was calculated from moles of hydrogen and acetylene as explained in section 4.2:

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

where dC_2H_2 = mole of acetylene in feed – mole of acetylene in product (iv)

dH_2 = mole of hydrogen in feed – mole of hydrogen in product (v)

mole of C_2H_2 is calculated by using (ii) whereas mole of H_2 can be measured employing the calibration curve of H_2 in Figure B.2, Appendix B., i.e.,

mole of H_2 = (area of H_2 peak from integrator plot on GC-8A) × 2.740×10^{-12} (vi)

APPENDIX D

CALCULATION FOR METAL ACTIVE SITES

Calculation of the metal active sites and metal dispersion of the catalyst measured by CO adsorption is as follows:

Let the weight of catalyst used = W g
Integral area of CO peak after adsorption = A unit
Integral area of 45 μl of standard CO peak = B unit
Amounts of CO adsorbed on catalyst = B-A unit
Volume of CO adsorbed on catalyst = $45\times[(B-A)/B]$ μl
Volume of 1 mole of CO at 30°C = 24.86×10^{6} μl
Mole of CO adsorbed on catalyst = $[(B-A)/B]\times[45/24.86\times10^{6}]$ mole
Molecule of CO adsorbed on catalyst = $[1.61\times10^{-6}]\times[6.02\times10^{23}]\times[(B-A)/B]$ molecules
Metal active sites = $9.68\times10^{17}\times[(B-A)/B]\times[1/W]$ molecules of CO/g of catalyst

APPENDIX E

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size calculated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{E.1}$$

where D = Crystallite size, Å

K = Crystallite-shape factor = 0.9

λ = X-ray wavelength, 1.5418 Å for CuKα

θ = Observed peak angle, degree

β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of a powder diffraction free from all broadening due to the experimental equipment. α-Alumina is used as a standard sample to observe the experimental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M^2 - B_S^2} \tag{E.2}$$

where B_M = The measured peak width in radians at half height.

B_S = The corresponding width of the standard material.

Example: Calculation of the crystallite size of α-alumina

The half-height width of peak = 0.30° (from Figure E.1)

= (2π x 0.30)/360

= 0.0052 radian

The corresponding half-height width of peak of of α-alumina (from the B_S value at the 2 theta of 43.32° in Figure E.2) = 0.0043 radian

$$\text{The pure width, } \beta = \sqrt{B_M^2 - B_S^2}$$

$$= \sqrt{0.0052^2 - 0.0043^2}$$

$$= 0.0029 \text{ radian}$$

B = 0.0029 radian

2θ = 43.32

θ = 21.66

λ = 1.5418 Å

$$\text{The crystallite size} = \frac{0.9 \times 1.5418}{0.0029 \cos 21.66} = 514.8 \text{ Å} = 51.5 \text{ nm}$$

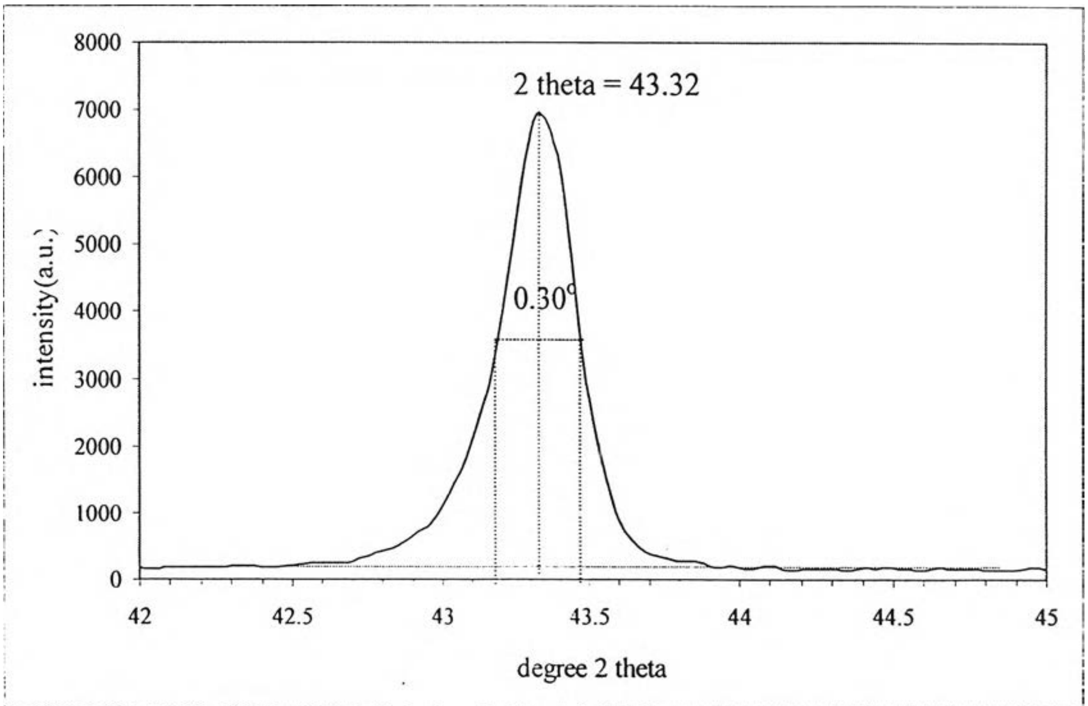

Figure E.1 The observation peak of α-alumina for calculating the crystallite size.

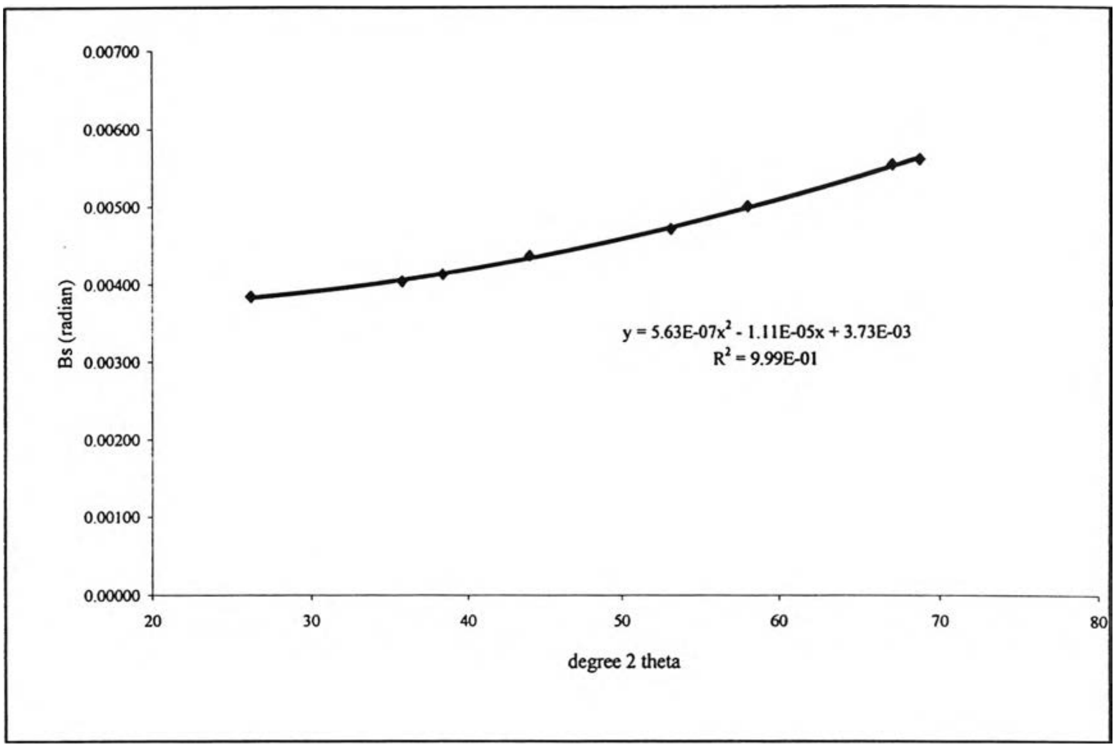

Figure E.2 The graph indicating that value of the line broadening attributeto the experimental equipment from the α-alumina standard.

APPENDIX F

CATALYST EVALUATION AS FUNCTION OF TEMPERATURE

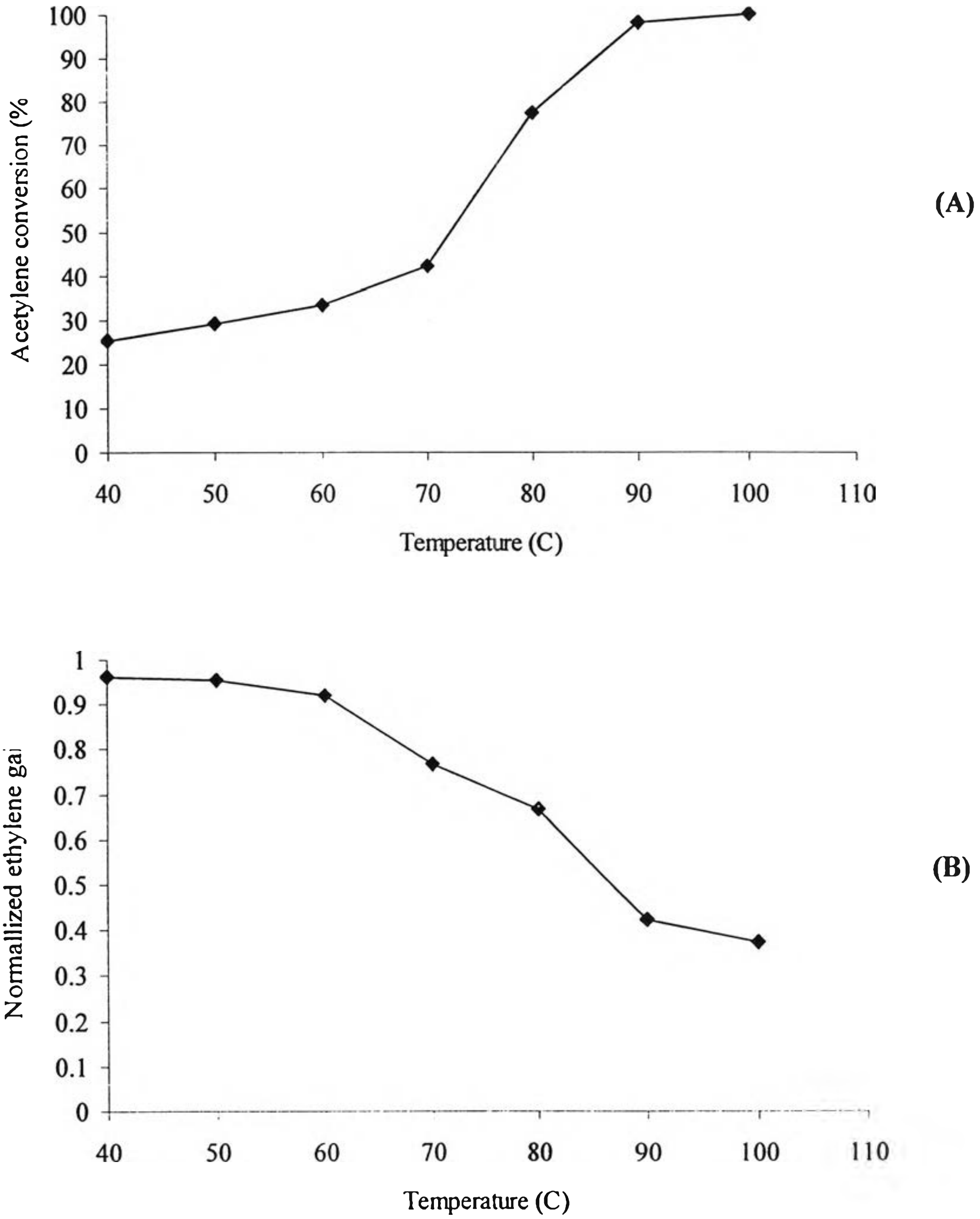

Figure F.1 Dependence of the catalytic performance of fresh commercial catalyst as a function of temperature: (A) % acetylene conversion and (B) normalized ethylene gain, GHSV, 5400 h^{-1}.

APPENDIX G

LIST OF PUBLICATIONS

1. Aungkapipattanachai, S., Sangvanich, T., Boonyaporn, P., Praserthdam, P., Panpranot, J., Study of Acetylene Hydrogenation Catalysts: Role of Coke Deposits. Proceeding of the Technology and Innovation for Sustainable Development Conference, January 25-27 (2006), Khon Kaen, Thailand.

Technology and Innovation for Sustainable Development Conference (TISD2006)
Faculty of Engineering, Khon Kaen University, Thailand
25-27 January 2006

Study of Acetylene Hydrogenation Catalysts: Role of Coke Deposits

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Abstract

Role of coke deposits, regeneration, and reactivation conditions on the properties of Pd-Ag/Al_2O_3 acetylene hydrogenation catalysts have been investigated. XRD analyses of fresh and spent catalysts indicated that there were no changes in the crystal size and phase of alumina after reaction. Temperature program oxidation study showed that more than one type of coke deposits existed on the catalyst surface and were completely burned off at temperature around 500-550°C. Oxygen concentration did not have a significant impact on catalyst regeneration since most of the catalyst active surface can be recovered after combustion at 500°C for 2 h in either O_2 1% or 21%. N_2O pretreatment can increased the active sites of the fresh Pd-Ag catalysts when reduced at 200°C. There was no such effect on the spent-regenerated catalysts. Reduction at 500°C also produced higher amount of active Pd surface than reduction at 200°C. Enhancement of acetylene conversion as well as ethylene gain was observed for N_2O-treated fresh Pd-Ag/Al_2O_3 catalyst. The N_2O pretreatment effect was much less pronounced when the spent-regenerated catalysts were employed.

Keywords: acetylene hydrogenation, coke deposits, Pd-Ag/Al_2O_3, catalyst

1. Introduction

Selective hydrogenation of acetylene in excess ethylene is an important process used to remove trace amounts of acetylene from ethylene feedstock in the production of polyethylene. An over-hydrogenation of ethylene to ethane has to be avoided while acetylene has to be reduced to a few ppm. Supported palladium catalysts are known to be the most selective for such reaction and usually employed in the industrial processes. However, catalytic activity and ethylene gain decrease with time-on-stream due to accumulation of large amounts of coke blocking the catalyst pores and inducing mass transfer limitations. Liu et al. [1] has found that steam alone cannot remove all deposited hydrocarbon on catalyst surface, and regeneration in air is needed to stripped hydrocarbon completely. The purposes of this study are to investigate the effects of amount of coke deposits and the conditions used for catalyst regeneration and activation on the performances of Pd-Ag/Al_2O_3 catalysts in selective acetylene hydrogenation. Various analytical techniques such as XRD, temperature-programmed oxidation, and CO-pulse chemisorption were applied.

2. Experimental

2.1 Catalyst

Fresh Pd-Ag catalysts used in this study are composed of 0.03wt% of Pd and 0.18wt% of Ag on α-Al_2O_3 and are denoted as Sample A. The BET surface area of the fresh catalyst is approximately 40 m^2/g. Spent catalysts with various wt% of coke deposits were obtained from an industrial C_2-reactor at different conditions and are denoted as samples B to E.

2.2 Catalyst Characterization

2.2.1 X-ray diffraction

The X-ray diffraction patterns of the catalysts with and without coke were carried out using an X-ray refractometer, SIEMENS D5000, with Cu K_α radiation, accurately measured in the 20–80° 2 theta angular region.

2.2.2 Determination of coke concentration

Samples with coke deposited were burned off in air at 500°C and the weight losses were measured. Reference sample of fresh catalyst was given the same treatment and the difference in weight loss was attributed to coke.

2.2.3 Temperature programmed oxidation

TPO was performed in a Micromeritic ChemiSorb 2750 automated system attached with ChemiSoft TPx software. Catalyst samples were packed in a u-shape quartz tube. To eliminate trace amount of water, the catalysts were heated in He to 200°C and holding at this temperature for 2 h and then cooled to room temperature. The sample was heated at the rate of 5°C/min in a 25 ml/min flow of 1%O_2 in

He.

2.2.4 CO chemisorption

The amounts of CO chemisorbed on the catalysts were measured using a Micromeritic ChemiSorb 2750 automated system. The sample was reduced in a H_2 flow at 200°C for 2 h then cooled down to ambient temperature in a He flow. When the treated catalysts were used, the samples were reduced with H_2, as mentioned above, then cooled down to the pretreatment temperature and held at that temperature for 10 min in a He flow before N_2O was introduced. CO-adsorption was measured after the reactor was cooled down to the ambient temperature.

2.2.5 Optical Microscope

Cross-sectional areas of the catalyst pellets were examined under a microscope. Pellet samples were prepared by grinding and polishing them with an ultra fine abrasive into disc shape with an approximate depth of 1 mm and then cleaning them by blowing. An Olympus SZX-12 optical microscope with a digital camera attached was used to take photographs of the magnified cross-sectional area of the catalyst pellets. The sample was placed under the specimen, and its photographs were taken at 20X magnification for observing the whole cross-section and at 45X for both the edge and the center.

2.3 Catalyst Regeneration and Activation

Regeneration was performed at 500°C for 2h in horizontal quartz tube with a 100ml/min flow of $1\%O_2$ or $21\%O_2$ in an inert. The catalysts were pretreated with or without N_2O prior to the reaction test. The catalysts were reduced in H_2 flow at 200°C for 2 h with a heating rate of °C/min, and then cooled down to the pretreatment temperature, 90°C [2] A small volume, 200µl/g of N_2O was injected into the system afterwards.

2.4 Reaction Study

Acetylene hydrogenation was performed in a 9 mm (i.d.) quartz tube reactor. Prior to the start of each run, the catalyst was reduced *in situ* with H_2 by heating from room temperature to 200°C at a heating rate of 10°C /min. Then the reactor was purged with argon and cooled down to the reaction temperature, 70°C. A feed composition of 1.4644% C_2H_2, 1.7052% H_2, 15.4695% C_2H_6 and balanced C_2H_4 with a GHSV of 5400 h^{-1} were used. The composition of product and feed stream were analyzed by a Shimadzu GC 8A equipped with TCD and FID detectors (molecular sieve-5A and carbosieve S-2 columns, respectively)

3. Results and Discussion

The XRD patterns of fresh and spent Pd-Ag/Al_2O_3 catalysts are shown in Figure 1. All the XRD peaks indicate the presence of alumina in both alpha and transition phases. No XRD peaks for palladium and silver oxides were observed due probably to the very low amount of the metals present on the catalysts and/or overlapping with the alumina peaks. XRD analyses of fresh and used catalysts indicated that there were no changes in phase of alumina after acetylene hydrogenation reaction.

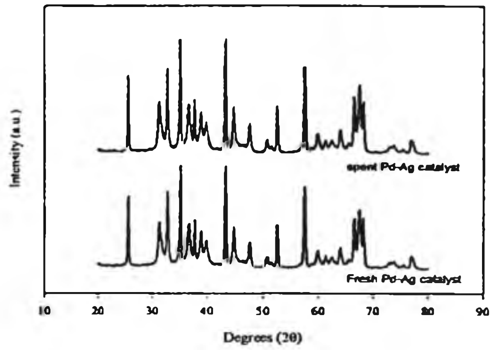

Figure 1 XRD patterns of fresh and spent Pd-Ag/Al_2O_3 catalysts

The amount of carbonaceous deposits on the spent catalysts was measured by temperature programmed oxidation technique and shown in **Figure 2**. After reaction, coke may deposit on the catalyst surface resulting in deactivation of the catalyst which can decrease the activity, selectivity and life time of the catalysts [3]. The amount of carbon deposits was found to be in the order of sample B < C < D < E. 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.

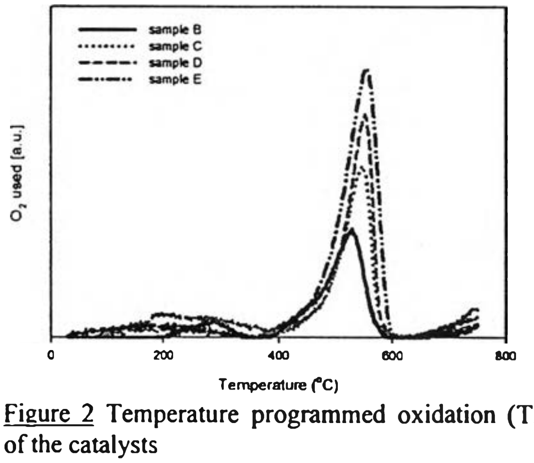

Figure 2 Temperature programmed oxidation (TPO) of the catalysts

Optical micrographs of cross-sectioned catalysts are shown in **Figure 3**. Coke formation was concentrated near the pellet periphery and appeared to be growing toward to the pellet center as %coke deposits increased. Coke concentrations in terms of wt% and amount of active sites measured by CO-pulse chemisorption are reported in **Table 1**. The results were in accordance to the TPO study. As %coke deposits increased the catalyst active sites decreased suggesting that the active surface of Pd were blocked by the carbon deposits.

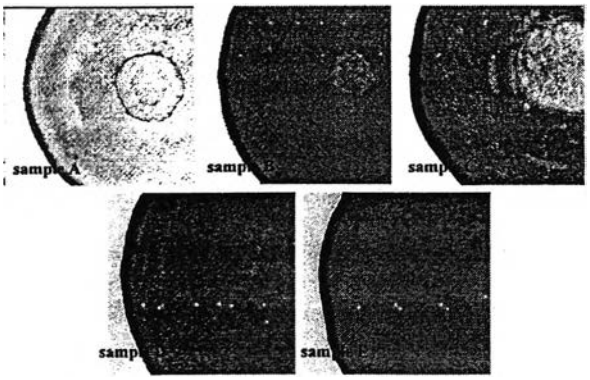

Figure 3 Optical micrographs of cross-sectioned Pd-Ag/Al_2O_3 catalysts

Table 1 Characteristics of Pd-Ag/Al_2O_3 catalysts

Sample	Coke concentration (wt%)	Active site (*10^{17}site/g cat.)
A (fresh)	0	2.76
B	0.18	1.54
C	0.24	0.58
D	0.28	0.29
E	0.54	Nil

The catalyst samples with coke deposits (sample B-E) were then regenerated at 500°C for 2 h using different O_2 concentration (1% and 21% O_2). After regeneration, catalyst active sites were measured again by CO chemisorption and results are given in **Table 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 sample E (the highest coke deposits) that regeneration was incomplete resulting in lower amount of active Pd sites. It is noted that CO was not adsorbed on Ag.

Table 2 Catalyst regeneration under different O_2 concentrations

Sample	Active site (*10^{-17}site/g cat.)	
	1% O_2	21% O_2
B	2.83	2.60
C	2.71	2.57
D	2.70	2.81
E	2.34	2.74

Catalyst active sites measured by CO chemisorption after activated by H_2 reduction at 200° and 500°C with and without N_2O pretreatment are shown in **Table 3**. The conditions used for N_2O pretreatment in this study were similar to those reported by Ngamsom et al. [2] to be the best conditions. It was found that N_2O pretreatment can increased the active sites of the fresh Pd-Ag catalysts when reduced at 200°C. During N_2O pretreatment accessible Pd sites responsible for acetylene hydrogenation to ethylene are enhanced while the sites for direct ethane formation are suppressed [4]. However, in this study we found that pretreatment of used catalysts did not result in the enhancement of Pd active sites. It is suggested that the changes in the catalyst geometry/morphology after being used in acetylene hydrogenation altered the N_2O pretreatment effect. In general, reduction at 500°C produced higher amount of active Pd surface than those reduced at 200°C due probably to larger amounts of PdO were able to be reduced.

Table 3 Active site of the catalyst after activation under different conditions (*10^{17}site/g cat.)

Sample	Reduced 200°C		Reduced 500°C	
	untreated	N_2O-treated	untreated	N_2O-treated
A	2.76	3.77	5.72	5.61
B	2.60	2.62	5.07	6.79
C	2.57	1.68	5.41	4.86
D	2.81	2.64	5.15	5.30
E	2.74	2.58	4.42	4.39

After regeneration and activation, the catalysts were tested for their catalytic performances in selective hydrogenation of acetylene in excess ethylene. The catalytic performance was evaluated in terms of acetylene conversion and ethylene gain (%) according to the following schemes:

$$C_2H_2 + H_2 \rightarrow C_2H_4$$
$$C_2H_4 + H_2 \rightarrow C_2H_6\text{, hence}$$

$$C_2H_2 + 2H_2 \rightarrow C_2H_6$$

Acetylene conversion is defined as mole of acetylene converted with respect to acetylene in feed. Ethylene gain is defined as:

$$\text{Ethylene gain} = \frac{C_2H_2 \text{ hydrogenated to } C_2H_4}{\text{Total hydrogenated } C_2H_2} \text{ x } 100$$

The ethylene being hydrogenated to ethane is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated thus:

$$\text{Ethylene gain} = \frac{[dC_2H_2 - (dH_2 - dC_2H_2)]}{dC_2H_2} x100$$

Or it can be written as:

$$\text{Ethylene gain} = (2 - \frac{dH_2}{dC_2H_2})x100$$

Acetylene conversion and ethylene gain of fresh (A) and regenerated catalyst samples (B) are shown in Figure 4 and 5, respectively.

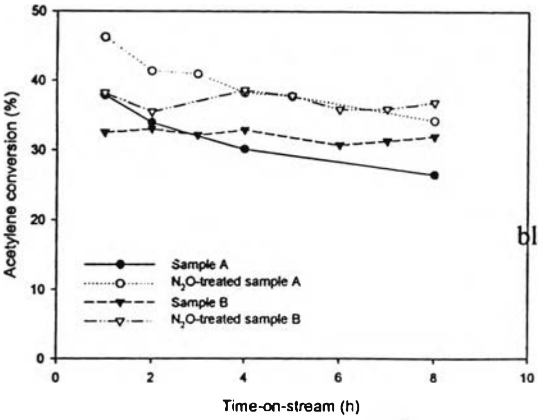

Figure 4 Acetylene conversions as a function of time-on-stream

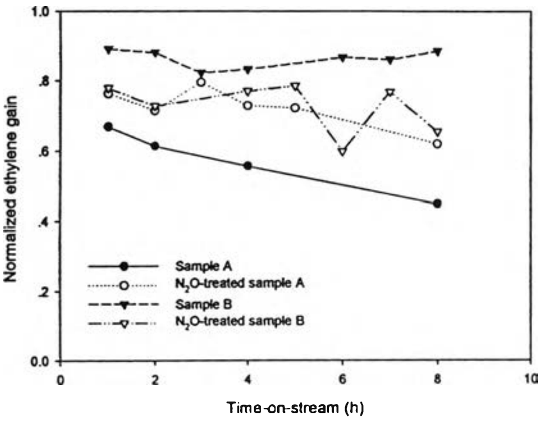

Figure 5 Ethylene gain as a function of time-on-stream

It can be seen that acetylene conversion as well as ethylene gain increased for N_2O-treated fresh Pd-Ag/Al_2O_3 catalyst. Acetylene conversion of the fresh catalyst was increased by 22%. The N_2O pretreatment effect was much less pronounced when the spent-regenerated catalysts were employed. Although, acetylene conversion of the used catalysts increased by 16%, ethylene gain decreased by 10%. The results suggest that there might be some changes in the catalyst properties after being used in acetylene hydrogenation reaction 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.

5. Conclusions

Amount of coke and oxygen concentration used in catalyst regeneration do not have a significant impact on the amount of active Pd surface recovered. However, study of catalyst activation by N_2O pretreatment revealed that there might be some changes in morphology or geometry of Pd and Ag on Al_2O_3 surface after used in acetylene hydrogenation thus only fresh catalysts were able to activate by N_2O.

Acknowledgments

This research was financially supported by the Rayong Olefins Co., Ltd and the Graduate School of Chulalongkorn University.

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VITA

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