



REFERENCES

- Albers, P., Pietsch, J., and Parker, S.F. (2001). Poisoning and deactivation of palladium catalysts. Journal of Molecular Catalysis A: Chemical, 173, 275-286.
- Alves, J.A., Bressa, S.P., Martinez, O.M., and Barreto, G.F. (2007). Kinetic study of liquid-phase hydrogenation of 1-butyne over a commercial palladium/alumina catalyst. Chemical Engineering Journal, 125, 131-138.
- Ardiaca, N.O., Bressa, S.P., Alves, J.A., Martinez, O.M., and Barreto, G.F. (2001). Experimental procedure for kinetic studies on egg-shell catalysts the case of liquid-phase hydrogenation of 1,3-butadiene and n-butenes on commercial Pd catalysts. Catalysis Today, 64, 205-215.
- Batista, J., Pintar, A., Gomilšek, J., Kodre, A., and Bornette, F. (2001). On the structural characteristics of γ -alumina-supported Pd-Cu bimetallic catalysts. Applied Catalysis A: General, 217, 55-68.
- Desiderio, R.J., Hirsig, A.R., and Miller, D.G. (1975). Selective hydrogenation of vinyl-acetylene. United States Patents.
- Ertl, G., Knozinger, H., Schth, F., and Weitkamp, J. (2008). Handbook of heterogeneous catalyst. weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
- Forzatti, P., and Lietti, L. (1999). Catalyst deactivation. Catalysis Today, 52, 165-181.
- Furlong, B.K., Hightower, J.W., and Chan, T.Y. (1994). Selective hydrogenation of 1,3-butadiene in 1-butene over alumina supported palladium and palladium/copper catalysts. Applied Catalysis A: General, 117, 41-51.
- Grant, J., Moyes, R., Oliver, R., and Well, P. (1976). The hydrogenation of alkadienes VII. 1,2-Butadiene hydrogenation catalyzed by two forms of nickel. Journal of Catalysis, 42, 213-220.
- Huang, W., McCormick, J., Lobo, R., and Chen, J. (2007). Selective hydrogenation of acetylene in the presence of ethylene on zeolite-supported bimetallic catalysts. Journal of Catalysis, 246, 40-51.

- Huang, W., Lobo, R., and Chen, J. (2008). Characterization of Na⁺- β -zeolite supported Pd and PdAg bimetallic catalysts using EXAFS, TEM and flow reactor. Journal of Molecular Catalysis A: Chemical, 283, 158-165.
- Kim, S., Lee, J., Ahn, I., Kim, W., and Moon, S. (2008). Performance of Cu promoted Pd catalysts prepared by adding Cu using a surface redox method in acetylene hydrogenation. Applied Catalysis A: General, 401, 12-19.
- Lederhos, C., Maccarrone, M., Badano, J., Torres, G., Coloma-Pascual, F., Yori, J., and Quiroga, M. (2011). Hept-1-yne partial hydrogenation reaction over supported Pd and W catalysts. Applied Catalysis A: General, 396, 170-176.
- Lieske, H., and Volter, J. (1985). Pd redispersion by spreading of PdO in O₂ treated Pd/Al₂O₃. Journal of Physical Chemistry, 89, 1841-1842.
- Meyer, E., and Burwell, R. (1963). The reaction between Deuterium and 1-Butyne, 1,2-Butadiene and 1,3-Butadiene on Pd-on-alumina. Journal of American Chemical Society, 85, 2881-2887.
- Miller, D., and Chuang, S. (2009). *In situ* infrared study of NO reduction over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts under H₂-rich and lean-burn conditions. Journal of the Taiwan Institute of Chemical Engineers, 40, 613-621.
- Pachulski, A., Schoedel, R., and Claus, P. (2011). Performance and regeneration studies of Pd-Ag/Al₂O₃ catalysts for the selective hydrogenation of acetylene. Applied Catalysis A: General, 400, 14-24
- Palinko, I. (1994). Effect of surface modifiers in the liquid phase hydrogenation of olefins over silica supported Pt, Pd and Rh catalysts II. thiophene and CS₂. Studies in the Surface Science and Catalysis, 88, 603-608.
- Pattamakomsan, K., Ehret, E., Morfin, F., Gelin, P., Jugnet, Y., Prakash, S., Bertolini, J., Panpranot, J., and Aires, F. (2010). Selective hydrogenation of 1,3-butadiene over Pd and Pd-Sn catalysts supported on different phases of alumina. Catalysis Today, 164, 28-33.
- Pattamakomsan, K., Suriye, K., Dokjampa, S., and Mongkolsiri, N. (2010). Effect of mixed Al₂O₃ structure between θ - and α -Al₂O₃ in the selective hydrogenation of 1,3-butadiene. Catalysis Communications, 11, 311-316.

- Pawelec, B., Cano-Serrano, E., Campos-Martin, J.M., Navarro, R.M., Thomas, S., and Fierro, J. (2004). Deep aromatics hydrogenation in the presence of DBT over Au–Pd/g-alumina catalysts. Applied Catalysis A: General, 275, 127-139.
- Ryndin, Y., Nosova, L., Boronin, A., and Chuvilin, A. (1988). Effect of dispersion of supported palladium on its electronic and catalytic properties in the hydrogenation of vinylacetylene. Applied Catalyst, 42, 131-141.
- Sarkany, A. (1997). Semi-hydrogenation of 1,3-butadiene on adspecies modified Pd—Ni, Co and Cu catalysts. Applied Catalysis A: General, 149, 207-223.
- Sarkany, A. (1997). Semi-hydrogenation of 1,3-butadiene over Pd-Ag/ α -Al₂O₃ poisoned by hydrocarbonaceous deposits. Applied Catalysis A: General, 165, 87-101.
- Sarkany, A., Horvath, A., and Beck, A. (2002). Hydrogenation of acetylene over low loaded Pd and Pd-Au/SiO₂ catalyst. Applied Catalysis A: General, 229, 117-125.
- Seth, D., Sarkar, A., Ng, F., and Rempel, G.L. (2007). Selective hydrogenation of 1,3-butadiene in mixture with isobutene on a Pd/ α -alumina catalyst in a semi-batch reactor. Chemical Engineering Science, 62, 4544-4557.
- Tew, M., Emerich, H., and Bokhoven, A. (2011). Formation and characterization of PdZn alloy: A very selective catalyst for alkyne semi-hydrogenation. The Journal of Physical Chemistry, 115, 8457-8465.
- Wongwaranon, N., Mekasuwandumrong, O., Praserthdam, P., and Panpranot, J. (2008). Performance of Pd catalysts supported on nanocrystalline α -Al₂O₃ and Ni-modified α -Al₂O₃ in selective hydrogenation of acetylene. Catalysis Today, 131, 553-558.
- Suo, Z., Ma, C., Jin, M., He, T., and An, L. (2008). The active phase of Au–Pd/Al₂O₃ for CO oxidation. Catalysis Communications, 9, 2187-2190.

APPENDICES

Appendix A The Catalytic Activity, 1,3-Butadiene Selectivity and 1-Butene Selectivity of Pd Catalysts

Table A1 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of 0.1% Pd catalyst

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5
Reaction time•wt of catalyst/wt of fed vinylacetylene (h)	0.07	0.14	0.21	0.28	0.35	0.42	0.49	0.56	0.63
Vinylacetylene conversion (%)	9.80	19.99	30.66	43.94	55.88	67.07	78.24	87.94	100
1,3-Butadiene selectivity (%)	41.61	48.85	49.10	50.11	46.23	43.14	34.43	24.38	8.87
1-Butene selectivity (%)	32.91	28.20	29.84	31.46	33.17	34.12	38.18	42.06	48.09

Table A2 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of 0.3% Pd catalyst

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5
Reaction time•wt of catalyst/wt of fed vinylacetylene (h)	0.06	0.12	0.17	0.23	0.29	0.35	0.41	0.47	0.52
Vinylacetylene conversion (%)	7.46	18.64	29.28	43.41	56.75	68.20	80.35	89.39	100
1,3-Butadiene selectivity (%)	85.93	67.18	73.97	67.00	59.15	60.79	45.30	34.94	15.73
1-Butene selectivity (%)	21.91	25.31	23.87	27.12	30.21	30.19	37.12	41.82	49.51

Table A3 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of 0.5% Pd catalyst

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Reaction time•wt of catalyst/wt of fed vinylacetylene (h)	0.06	0.12	0.18	0.24	0.30	0.36	0.41	0.47
Vinylacetylene conversion (%)	11.03	25.39	36.21	50.10	63.86	76.77	88.03	100
1,3-Butadiene selectivity (%)	56.78	49.90	56.19	51.98	45.90	42.57	25.95	14.62
1-Butene selectivity (%)	26.68	27.97	29.91	31.35	35.56	37.30	46.99	47.32

Table A4 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of 0.7% Pd catalyst

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Reaction time•wt of catalyst/wt of fed vinylacetylene (h)	0.06	0.12	0.18	0.23	0.29	0.35	0.41	0.47
Vinylacetylene conversion (%)	11.57	25.82	40.38	55.51	71.18	84.31	93.68	100
1,3-Butadiene selectivity (%)	63.94	58.63	54.33	51.24	44.82	34.60	20.45	-3.56
1-Butene selectivity (%)	21.32	26.90	29.83	32.09	35.52	41.00	47.87	52.89

Table A5 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of 1.0% Pd catalyst

Reaction time (h)	0.5	1	1.5	2	2.5	3
Reaction time•wt of catalyst/wt of fed vinylacetylene (h)	0.07	0.14	0.21	0.29	0.36	0.43
Vinylacetylene conversion (%)	18.26	37.72	57.73	77.93	92.19	100
1,3-Butadiene selectivity (%)	47.53	47.19	42.94	31.98	11.44	-19.96
1-Butene selectivity (%)	30.47	33.72	36.59	42.23	53.03	49.75

Appendix B The Catalytic Activity, 1,3-Butadiene Selectivity and 1-Butene Selectivity of Pd-Cu Catalysts

Table B1 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 0.25

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0001	0.0003	0.0005	0.00061	0.00077	0.00092	0.00107	0.00123	0.00138	0.00153	0.00169	0.00184	0.00199	0.00215	0.0023	0.00245
Vinylacetylene conversion (%)	4.52	10.27	16.35	23.01	29.75	37.30	44.88	52.56	60.14	67.56	74.72	81.40	87.51	93.19	96.84	100
1,3-Butadiene selectivity (%)	52.44	47.64	52.77	51.91	50.40	49.23	47.84	46.18	44.61	42.49	39.55	36.48	32.22	26.23	17.63	8.52
1-Butene selectivity (%)	29.24	27.77	30.11	30.35	31.62	31.78	32.30	33.08	33.71	34.81	36.36	38.02	40.14	43.05	47.41	50.35

Table B2 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 0.50

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.00021	0.00043	0.00064	0.00086	0.00107	0.00128	0.0015	0.00171	0.00193	0.00214
Vinylacetylene conversion (%)	6.95	18.53	31.11	43.31	56.05	68.30	79.64	89.47	96.14	100
1,3-Butadiene selectivity (%)	76.18	53.01	52.26	50.89	47.03	43.40	39.07	29.94	17.60	-8.86
1-Butene selectivity (%)	21.92	28.09	28.63	29.54	31.91	34.06	36.47	41.52	47.78	54.79

Table B3 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.0

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0005	0.0007	0.0009	0.0011	0.0013	0.0015
Vinylacetylene conversion (%)	11.83	27.42	41.27	56.06	70.86	83.56	93.46	100
1,3-Butadiene selectivity (%)	43.67	41.38	45.15	42.96	36.47	30.28	18.63	-6.78
1-Butene selectivity (%)	30.37	30.24	31.80	33.52	37.77	41.50	47.87	55.77

Table B4 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0001	0.0003	0.0004	0.0006	0.0007	0.0008	0.001	0.0011	0.0012
Vinylacetylene conversion (%)	9.29	21.03	34.88	49.99	64.10	77.81	89.51	97.04	100
1,3-Butadiene selectivity (%)	53.85	53.88	50.11	45.36	43.58	37.84	28.45	11.19	-25.98
1-Butene selectivity (%)	27.93	28.19	30.07	32.52	33.68	37.03	42.12	50.48	53.62

Table B5 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 2.0

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0005	0.0007	0.0009	0.0011	0.0012	0.0014	0.0016	0.0018
Vinylacetylene conversion (%)	9.35	21.08	33.12	45.65	57.80	70.01	80.98	90.23	96.43	100
1,3-Butadiene selectivity (%)	57.52	50.35	47.85	45.97	44.00	39.29	34.24	24.85	10.08	-11.81
1-Butene selectivity (%)	25.45	29.03	30.67	31.96	33.10	35.82	38.67	43.58	50.39	52.26

Appendix C The Catalytic Activity, 1,3-Butadiene Selectivity and 1-Butene Selectivity of Pd-Cu Catalysts with Pd/Cu Ratio of 1.5 at Various Reaction Temperature

Table C1 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 27 °C and 4.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0006	0.0008	0.001	0.0012	0.0014	0.0016	0.0018	0.002	0.0022
Vinylacetylene conversion (%)	9.25	20.03	32.77	42.91	54.02	64.43	74.12	82.66	89.79	95.41	100
1,3-Butadiene selectivity (%)	43.16	48.17	51.27	49.10	47.34	42.74	38.87	31.31	21.70	6.69	-15.16
1-Butene selectivity (%)	28.63	29.85	28.88	30.84	32.24	35.54	37.92	42.53	47.25	54.71	56.64

Table C2 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 35 °C and 4.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0006	0.0008	0.001	0.0012	0.0013	0.0015	0.0017	0.0019
Vinylacetylene conversion (%)	11.51	24.42	37.70	50.85	63.58	75.26	85.28	93.00	98.04	100
1,3-Butadiene selectivity (%)	52.46	50.68	49.99	47.29	42.83	37.32	27.88	13.70	-7.68	-43.72
1-Butene selectivity (%)	28.08	29.50	30.23	32.10	34.70	38.03	43.04	50.25	55.95	55.07

Table C3 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 43 °C and 4.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0006	0.0008	0.001	0.0012	0.0013	0.0015
Vinylacetylene conversion (%)	14.17	29.68	46.21	61.57	75.11	87.78	96.12	100
1,3-Butadiene selectivity (%)	53.51	51.45	47.17	43.31	36.69	26.01	7.12	-23.95
1-Butene selectivity (%)	28.15	29.52	31.29	33.50	37.86	43.14	52.13	54.54

Appendix D The Catalytic Activity, 1,3-Butadiene Selectivity and 1-Butene Selectivity of Pd-Cu Catalysts with Pd/Cu Ratio of 1.5 under Various H₂ Pressure

Table D1 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 35 °C and 3.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0005	0.0007	0.0009	0.0011	0.0012	0.0014	0.0016	0.0018	0.002	0.0021	0.0023
Vinylacetylene conversion (%)	8.014	16.7	26.08	35.72	45.14	54.71	63.73	72.58	80.47	87.55	93.22	97.23	100
1,3-Butadiene selectivity (%)	56.82	55.97	53.77	52.31	50.32	48.14	45.6	42.65	38.23	31.75	22.65	9.497	-9.94
1-Butene selectivity (%)	27.24	27.49	28	29.09	29.81	31.03	32.46	34.43	36.77	40.4	45.19	51.74	55.27

Table D2 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 35 °C and 4.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0006	0.0008	0.001	0.0012	0.0013	0.0015	0.0017	0.0019
Vinylacetylene conversion (%)	11.51	24.42	37.7	50.85	63.58	75.26	85.28	93	98.04	100
1,3-Butadiene selectivity (%)	52.46	50.68	49.99	47.29	42.83	37.32	27.88	13.7	-7.68	-43.7
1-Butene selectivity (%)	28.08	29.5	30.23	32.1	34.7	38.03	43.04	50.25	55.95	55.07

Table D3 The catalytic activity, 1,3-butadiene selectivity and 1-butene selectivity of Pd-Cu catalyst with Pd/Cu ratio of 1.5 at 35 °C and 5.5 bar H₂

Reaction time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Reaction time•wt of Pd/wt of fed vinylacetylene (h)	0.0002	0.0004	0.0005	0.0007	0.0009	0.0011	0.0012	0.0014
Vinylacetylene conversion (%)	15.07	32.23	48.93	64.85	78.78	89.87	97.19	100
1,3-Butadiene selectivity (%)	53.22	48.49	45.36	39.27	27.89	11.2	-14.5	-82.7
1-Butene selectivity (%)	29.91	33.54	34.83	38.2	44.4	52.4	56.5	42.5

CURRICULUM VITAE

Name: Mr. Katawut Choochuen

Date of Birth: August 27, 1987

Nationality: Thai

University Education:

2006-2009 Bachelor degree of Engineering in Major of Petrochemical and Polymeric material, Faculty of Engineering and Industrial Technology, Silpakorn university, Nakorn Pathom, Thailand.

Working Experience:

2008 Position: Internship Student
 Company name: Thaiparaxylene Co., Ltd.

Proceedings:

Choochuen, K., Inson, P., Kitiyanan, B., and Schwank, J. (2012, April 24) Selective Hydrogenation of Vinylacetylene in Mixed C4 Using Pd-Cu on Alumina Catalyst. Proceedings of the 18th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

Presentations:

Choochuen, K., Inson, P., Kitiyanan, B., and Schwank, J. (2012, April 24) Selective Hydrogenation of Vinylacetylene in Mixed C4 Using Pd-Cu on Alumina Catalyst. Poster presented at the 18th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

