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.

Álvarez-Galván, M. C., Pawelec, B., de la Peña O'Shea, V. A., Fierro, J. L. G., and Arias, P. L. (2004) Formaldehyde/methanol combustion on alumina-supported manganese-palladium oxide catalyst. Applied Catalysis B: Environmental, 51, 83-91.

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.

Alvez-Manoli., G., Pinnavaia, T. J., Zhang, Z., Lee, D. K., Marin-Astorga, K., and Rodriguez, P. (2010) Stereo-selective hydrogenation of 3-hexyne over low-loaded palladium catalysts supported on mesostructured materials. Applied Catalysis A: General, 387, 26-34.

Anderson, J. A., Mellor, J., and Wells, R. P. K. (2009) Pd catalyzed hexyne hydrogenation modified by Bi and by Pb. Journal of Catalysis, 261, 208-216.

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.

Beamson, G., Papworth, A. J., Philipps, C., Smith, and A. M., and Whyman, R. (2011) Selective hydrogenation of amides using bimetallic Ru/Re and Rh/Re catalysts. Journal of Catalysis, 278, 228-238.

Choochoen, K. (2012) Selective hydrogenation of vinylacetylene in mixed C4 using Pd-Cu on alumina catalyst. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

Crespo-Quesada, M., Dykeman, R. R., Laurenczy, G., Dyson, P. J., and Minsker, L. K. (2011) Supported nitrogen-modified Pd nanoparticles for the selective hydrogenation of 1-hexyne. Journal of Catalysis, 279, 66-74.

Desiderio, R. J., Hirsig, A. R., and Miller, D. G. (1975) Selective hydrogenation of vinyl-acetylene. U.S. Patent 3 898 298.

Forzatti, P., and Lietti, L. (1990) Catalyst deactivation. Catalyst 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 alkadienesVII. 1,2-Butadiene hydrogenation catalyzed by two forms of nickel. Journal of Catalysis, 42, 213-220.

Han, X. X., Zhou, R. X., Lai, G. H., Yue, B. H., and Zheng, X. M. (2004) Effect of transition metal (Cr, Mn, Fe, Co, Ni and Cu) on the hydrogenation properties of chloronitrobenzene over Pt/TiO_2 catalysts. Journal of Molecular Catalysis A: Chemical, 209, 83–87.

Han, X. X., Chen, Q., and Zhou, R. X. (2007) Study on the hydrogenation of *p*-chloronitrobenzene over carbon nanotubes supported platinum catalysts modified by Mn, Fe, Co, Ni and Cu. Journal of Molecular Catalysis A: Chemical, 277, 210–214.

Hong, Y. K., Lee, D. W., Eom, H. J., and Lee, K. Y. (2014) The catalytic activity of Pd/WOX/Y-Al2O3 for hydrodeoxygenation of guaiacol. Applied Catalysis B: Environmental, 150-151, 438-445.

Huang, W., McCormick, J., Lobo, R., and Chen, J. (2007) Selective hydrogenation of acetylene in the presence of ethylene on Al_2O_3 and β-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.

Karavanov, A. N., Gryaznov, V. M., Lebedeva, V. I., Litvinov, I. A., Vasil'kov b, A.Yu., Olenin, and A.Yu. (1995) Porous membrane catalysts with Pd-M-clusters for liquid phase hydrogenation of dehydrolinalool. Catalysis Today, 25, 447-450.

Kim, S., Lee, J., Ahn, I., Kim, W., and Moon, S. (2008) Performance of Cu promoted Pd catalyst prepared by adding Cu using a surface redox method in acetylene hydrogenation. Applied Catalysis A: General, 401, 12-19.

Kittisakmontree, P., Pongthawornsakun, B., Yoshida, H., Fujita, S. I., Arai, M., and Panpranot, J. (2013) The liquid-phase hydrogenation of 1-heptyne over Pd-Au/TiO_2 catalysts prepared by the combination of incipient wetness impregnation and deposition–precipitation. Journal of Catalysis, 297, 155-164.

Lederhos, C., Badano, J., Quiroga, M., and L'Argentière, P. (2010) Influence of Ni addition to a low-loaded palladium catalyst on the selective hydrogenation of 1-heptyne. Química Nova, 33, 816-820.

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.

Liprandi, D. A., Cagnola, E. A., Paredes, J. F., Badano, J. M., and Quiroga, M. E. (2012) A high (Z)/(E) ratio obtained during the 3-hexyne hydrogenation with a catalyst based on a Rh(I) complex anchored on a carbonaceous support. Catalysis Letter, 142, 231-237.

Maccarrone, M. J., Lederhos, C. R., Torres, G., Betti, C., Pascual, F. C., Quiroga, M. E., and Yori, J. C. (2012) Partial hydrogenation of 3-hexyne over low-loaded palladium mono and bimetallic catalysts. Applied Catalysis A: General, 441-442, 90-98.

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 the American Chemical Society, 85, 281-288.

Naumkin, A., Kraut-Vass, A., Gaarenstroom, S., and Powell, C. (1996) Enhanced adherence of area-selective electroless metal plating on insulators. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 14, 319-326.

Ngamsom, B., Bogdanchikova, N., Borja, M. A., and Praserthdam, P. (2004) Characterisations of Pd–Ag/Al_2O_3 catalysts for selective acetylene hydrogenation: effect of pretreatment with NO and N_2O. Catalysis Communications, 5, 243-248.

Pachulski, A., Schoedel, R., and Claus, P. (2011) Performance and regeneration studies of Pd-Ag/Al_2O_3 catalysts for the selective hydrogenation of acetylene. Applied Catalysis A: General, 400, 14-24.

Pattamakomsan, K., Ehret,E., Morfin,F., Gelin, P., Jugnet,Y., Prakash, S., Bertolini, J.C., Panpranot, J., and Aires, F.J.C.S. (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 Al_2O_3 structure between θ- and α-Al_2O_3 on the properties of Pd/Al_2O_3 in the selective hydrogenation of 1,3-butadiene. Catalysis Communications, 11, 311-316.

Ryndin, Y. A., Nosova, L.V., Boronin, A. I., and Chuvilin, A. L. (1988) Effect of dispersion of supported palladium on its electronic and catalytic properties in the hydrogenation of vinylacetylene. Applied Catalysis, 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-Al_2O_3 poisoned by hydrocarbonaceous deposits. Applied Catalysis A: General, 229, 117-125.

Sarkany, A., Horvath, A., and Beck, A. (2002) Hydrogenation of acetylene over low loaded Pd and Pd-Au/SiO_2 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.

Suriyaphaparkorn, K. (2013) Selective hydrogenation of 1-hexyne using low loaded Pd, Pd-Cu and Pd-W supported on alumina catalyst. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

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.

Tew, M., Janousch, M., Huthwelker, T., and van Bokhoven, J. (2011) The roles of carbide and hydride in oxide-supported palladium nanoparticles for alkyne hydrogenation. Journal of Catalysis, 283, 45-54.

Wongwaranon, N., Mekasuwandumrong, O., Praserthdam, P., and Panpranot, J. (2008) Performance of Pd catalysts supported on nanocrystalline α-$Al_2O_3$and Ni-modified α-Al_2O_3 in selective hydrogenation of acetylene. Catalysis Today, 131, 553-558.

Zhou, X., Sun, H., Guo, W., Liu, Z., and Liu, S. (2011) Selective hydrogenation of benzene to cyclohexene on Ru-based catalysts promoted with Mn and Zn. Journal of Natural Gas Chemistry, 20, 53–59.

APPENDICES

Appendix A The Catalytic Activity of 1-Hexyne, 1-Hexene Selectivity and *n*-Hexane Selectivity of 0.3 wt% Pd and Pd-Mn Supported on Alumina Catalysts

Table A1 The peak area and mole of components for calibration curve

Wt% of components	Peak area			Mole of Components		
	C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}
0.5	343.5	318.3	356.4	2.04E-8	1.98E-8	1.97E-8
1	645.7	673.6	693.4	4.08E-8	3.96E-8	3.93E-8
2.5	1747.4	1720.0	1747.7	1.02E-7	9.91E-8	9.83E-8

Table A2 The slope of calibration curve

Components	Slope of calibration curve
Hexyne	1.69E10
Hexene	1.73E10
Hexane	1.78E10

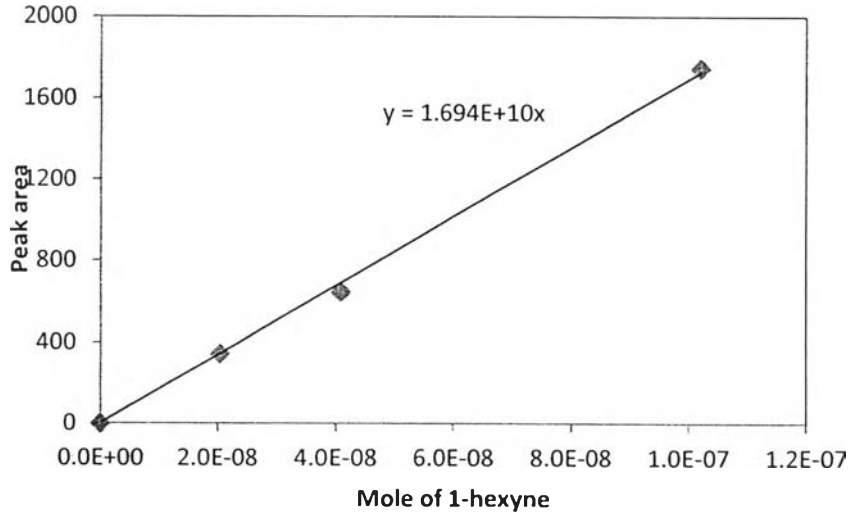

Figure A1 The calibration curve of 1-hexyne.

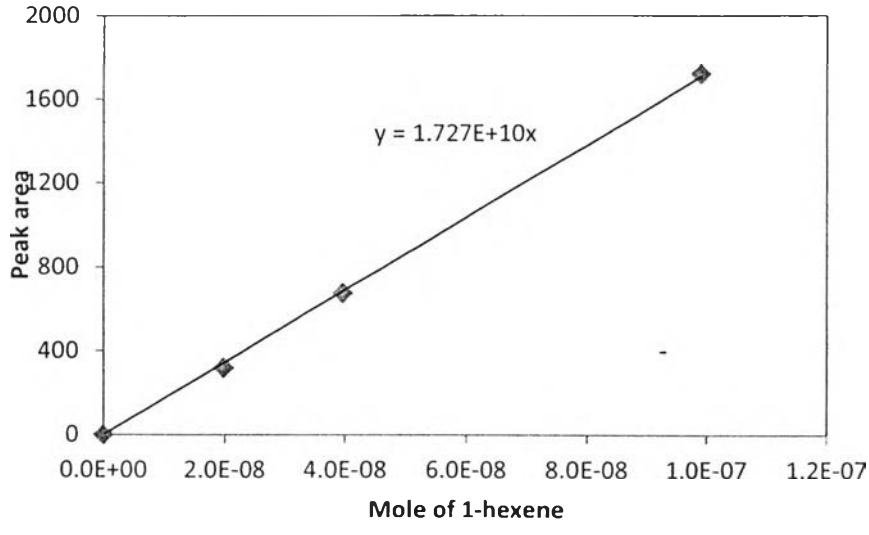

Figure A2 The calibration curve of 1-hexene.

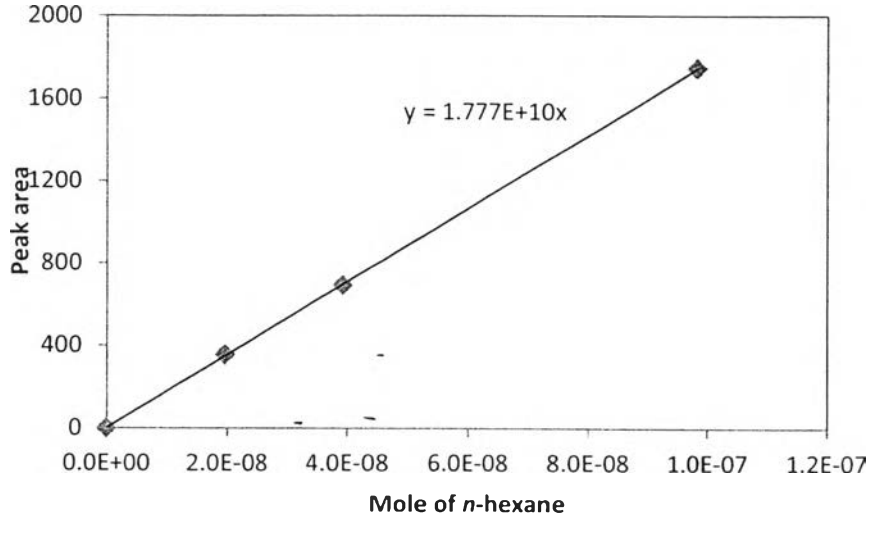

Figure A3 The calibration curve of *n*-hexane.

Table A3 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
815.2	498.6	24.7	4.8E-8	2.9E-8	1.4E-9	41.8	83.5	2.6	34.9
385.9	764.4	27.5	2.3E-8	4.4E-8	1.6E-9	72.5	73.9	4.0	53.5
27.3	806.7	28.4	1.6E-9	4.7E-8	1.6E-9	98.1	57.6	4.4	56.5
0.0	705.8	38.7	0.0	4.1E-8	2.2E-9	100.0	49.5	5.2	49.4
0.0	625.1	65.1	0.0	3.6E-8	3.7E-9	100.0	43.8	7.9	43.8

Table A4 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 0.5

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
515.2	708.8	0.0	3.0E-8	4.1E-8	0.0	58.4	96.0	0.0	56.1
20.2	1068.2	10.3	1.2E-9	6.2E-8	5.8E-10	98.4	86.0	0.9	84.5
0.0	926.9	201.8	0.0	5.4E-8	1.1E-8	100.0	73.3	15.5	73.3
0.0	852.7	345.9	0.0	4.9E-8	2.0E-8	100.0	67.5	26.6	67.5
0.0	774.5	421.9	0.0	4.5E-8	2.4E-8	100.0	61.3	32.4	61.3

Table A5 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 0.75

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
517.8	856.3	3.4	3.1E-8	5.0E-8	1.9E-10	63.0	95.1	0.4	60.0
23.6	1208.6	9.4	1.4E-9	7.0E-8	5.3E-10	98.3	86.1	0.7	84.6
0.0	1064.2	235.7	0.0	6.2E-8	1.3E-8	100.0	74.5	16.0	74.5
0.0	979.2	400.1	0.0	5.7E-8	2.3E-8	100.0	68.6	27.2	68.6
0.0	863.2	522.6	0.0	5.0E-8	2.9E-8	100.0	60.4	35.6	60.4

Table A6 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 1.0

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
233.0	1007.3	8.6	1.4E-8	5.8E-8	4.8E-10	81.2	98.2	0.8	79.7
0.0	1128	81.5	0.0	6.5E-8	4.6E-9	100.0	89.3	6.3	89.3
0.0	998.4	224.1	0.0	5.8E-8	1.3E-8	100.0	79.0	17.2	79.0
0.0	895.3	363.2	0.0	5.2E-8	2.0E-8	100.0	70.8	27.9	70.8
0.0	820.4	447.6	0.0	4.8E-8	2.5E-8	100.0	64.9	34.4	64.9

Table A7 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 1.5

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
768.9	463.4	5.6	4.5E-8	2.7E-8	3.2E-10	38.0	96.6	1.1	36.7
401.8	772.1	10.6	2.4E-8	4.5E-8	6.0E-10	67.6	90.4	1.2	61.1
35.8	985.2	29.7	2.1E-9	5.7E-8	1.7E-9	97.1	80.3	2.4	78.0
0.0	935.8	194.8	0.0	5.4E-8	1.1E-8	100.0	74.0	15.0	74.0
0.0	845.3	267.5	0.0	4.9E-8	1.5E-8	100.0	66.9	20.6	66.9

Table A8 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 2.0

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
842.8	395.7	7.8	5.0E-8	2.3E-8	4.4E-10	32.0	97.8	1.9	31.3
535.4	661.1	17.3	3.2E-8	3.8E-8	9.7E-10	56.8	92.1	2.3	52.3
90.2	953.9	35.7	5.3E-9	5.5E-8	2.0E-9	92.7	81.4	3.0	75.5
0.0	948.6	160.2	0.0	5.5E-8	9.0E-9	100.0	75.1	12.3	75.1
0.0	850.2	200.0	0.0	4.9E-8	1.1E-8	100.0	67.3	15.4	67.3

Table A9 The peak area, mole of components, catalytic activity, 1-hexene selectivity, *n*-hexane selectivity and 1-hexene yield for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 wt% Pd/Al_2O_3 at Pd/Mn = 5.0

Peak area			Mole of Components			Conv (%)	C_6H_{12} Sel (%)	C_6H_{14} Sel (%)	C_6H_{12} Yld (%)
C_6H_{10}	C_6H_{12}	C_6H_{14}	C_6H_{10}	C_6H_{12}	C_6H_{14}				
1013.1	384.8	8.1	6.0E-8	2.2E-8	4.6E-10	27.7	97.4	2.0	27.0
645.7	701.4	20.2	3.8E-8	4.1E-8	1.1E-9	53.9	91.1	2.6	49.1
193.7	1008.3	38.6	1.1E-8	5.8E-8	2.2E-9	86.2	81.9	3.1	70.6
0.0	1082.1	189.5	0.0	6.3E-8	1.1E-8	100.0	75.8	12.9	75.8
0.0	951.2	294.7	0.0	5.5E-8	1.7E-8	100.0	66.6	20.1	66.6

Appendix B The Mole Fraction of 1-Hexyne, 1-Hexene and *n*-Hexane for 1-Hexyne Hydrogenation of 0.3 wt% Pd and Pd-Mn Supported on Alumina Catalysts

Table B1 The mole fraction for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 %wt Pd/Al_2O_3

Time (h)	Mole fraction		
	C_6H_{10}	C_6H_{12}	C_6H_{14}
0	1.00	0.00	0.00
1	0.61	0.37	0.02
2	0.33	0.65	0.02
3	0.03	0.94	0.03
4	0.00	0.95	0.03
5	0.00	0.91	0.09

Table B2 The mole fraction for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 %wt Pd/Al_2O_3 at Pd/Mn = 0.5, 0.75 and 1.0

Time (h)	Pd/Mn = 0.5			Pd/Mn = 0.75			Pd/Mn = 1.0		
	Mole fraction								
	C_6H_{10}	C_6H_{10}	C_6H_{14}	C_6H_{12}	C_6H_{14}	C_6H_{12}	C_6H_{14}	C_6H_{12}	C_6H_{14}
0	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00
1	0.43	0.57	0.00	0.38	0.62	0.00	0.19	0.80	0.01
2	0.02	0.97	0.01	0.02	0.97	0.01	0.00	0.93	0.07
3	0.00	0.82	0.17	0.00	0.82	0.18	0.00	0.82	0.18
4	0.00	0.72	0.28	0.00	0.72	0.28	0.00	0.72	0.28
5	0.00	0.65	0.35	0.00	0.63	0.37	0.00	0.65	0.35

Table B3 The mole fraction for the hydrogenation of 1-hexyne at 40 °C and 1.5 bar over 0.3 %wt Pd/Al_2O_3 at Pd/Mn = 1.5, 2.0 and 5.0

Time (h)	Pd/Mn = 1.5			Pd/Mn = 2.0			Pd/Mn = 5.0		
	Mole fraction								
	C_6H_{10}	C_6H_{10}	C_6H_{14}	C_6H_{12}	C_6H_{14}	C_6H_{12}	C_6H_{14}	C_6H_{12}	C_6H_{14}
0	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00
1	0.63	0.37	0.00	0.68	0.31	0.01	0.72	0.27	0.01
2	0.34	0.65	0.01	0.45	0.54	0.01	0.48	0.51	0.01
3	0.03	0.94	0.03	0.09	0.88	0.03	0.16	0.81	0.03
4	0.00	0.83	0.17	0.00	0.86	0.14	0.00	0.85	0.15
5	0.00	0.76	0.24	0.00	0.81	0.19	0.00	0.77	0.23

Appendix C Hydrogen Chemisorption of 0.3 %wt Pd and Pd-Mn supported on alumina catalysts

Table C1 H_2 chemisorption results of 0.3 wt% Pd/Al_2O_3 catalysts at various Mn loadings

Catalysts	H/Pd
Pd/Al_2O_3	0.3381
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 0.5)	0.1875
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 0.75)	0.2015
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 1.0)	0.2154
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 1.5)	0.1738
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 2.0)	0.1541
$Pd\text{-}Mn/Al_2O_3$ (Pd/Mn = 5.0)	0.1439

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Presentation:

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