

Selective hydrogenation of 2-methyl-3-butyn-2-ol over Pd/ZnO: Pd-Zn synergistic study

*Fernando Cárdenas-Lizana, Micaela Crespo-Quesada and Lioubov Kiwi-Minsker**

Group of Catalytic Reaction Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL),

CH-1015 Lausanne, Switzerland

** Corresponding author: EPFL-SB-ISIC-GGRC, Station 6; lioubov.kiwi-minsker@epfl.ch; 0041 21 693 3182; 0041 21 693 3667.*

Abstract

Graphical abstract

Supported *N*-modified Pd nanoparticles selectively catalyze 1-hexyne hydrogenation to 1-hexene, demonstrating a remarkable increase of the selectivity through a site-blocking effect and complete hindering of the over-hydrogenation to 1-hexane.

Keywords:

1 Introduction

About 20% of the reactions used to produce fine chemicals and pharmaceuticals are hydrogenations [1]. Supported Pd nanoparticles (NPs) are known to selectively catalyze the hydrogenation of alkynes to alkenes [2]. The yield of the alkene hydrogenation product increases considerably when modifiers are added to the reaction mixture.

In the studies reported herein, an in-house synthesized imidazolium tagged bipy ligand and bipy itself were used in the synthesis of monodispersed Pd NPs with a dual aim: stabilizing the nanoparticles by anchoring them to the support and inducing a permanent modification of the surface. To the best of our knowledge, the combination of a functionalized structured support and a tailored-made ligand capable of strongly interacting in order to minimize leaching while increasing selectivity has not been previously reported. The resulting catalysts were tested in the liquid-phase hydrogenation of 1-hexyne in *n*-heptane and their performance was compared to that of a reference Pd/CNF/SMF catalyst, prepared by a conventional ion-exchange method [25], in

the absence of modifiers. The catalysts were further characterized by Scanning and Transmission Electron Microscopy (SEM and TEM), X-Ray Photoelectron Spectroscopy (XPS) and CO-chemisorption in order to rationalize the catalytic response observed.

2 Materials and methods

2.1 *Materials*

2.2 *Preparation of the Pd/CNF/SMF reference catalyst*

2.3 *N-modified Pd catalyst preparation*

2.4 *Hydrogenation reactions*

2.5 *Characterization techniques*

3 Results and discussion

3.1 *Catalysts used in this work*

4. Conclusions

N-modified Pd NPs immobilized on CNF/SMF supports were synthesized and studied in the selective hydrogenation of 1-hexyne. Compared to a reference catalyst, selectivity to 1-hexene increased from 83% to 98% near full conversion. Furthermore, the over-hydrogenation to n-hexane was largely suppressed in the presence of N-modified Pd NPs.

A Langmuir-Hinshelwood model was found to be consistent with the observed reaction kinetics and showed that the N-contained ligands permanently adsorb on the Pd surface “blocking” the active sites for 1-hexene adsorption. Nonetheless, an electronic effect from the N-coordinated Pd²⁺ species resulting in a change in the adsorption strengths and kinetic constants also contributes to the change in the catalytic performance. Moreover, the imidazolium functionalized ligand was found to reduce Pd leaching from the catalyst presumably due to a stronger ionic interaction with the oxygenated surface groups present on the CNF.

Acknowledgements

The Swiss National Science Foundation is acknowledged for financial support. The authors also thank Nicolas Xanthopoulos (EPFL-SB-CIME) for the XPS measurements.

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Schemes

Scheme 1

Scheme 2

Figure and scheme captions

Fig. 1.

Scheme 1.

Table 1. Catalysts used during this work.					
Catalyst	Stabilizer	NP synthesis in	IL coating	%Pd ^b	% IL
Reference	-	-	-	0.6 ^b	-
Reference	-	-	[bmim][PF ₆]	0.82 ^b	4.2
Reference	-	-	[C ₂ OHmim][BF ₄]	0.48 ^b	5.4
Reference	-	-	[C ₂ CNmim][Tf ₂ N]	0.62 ^b	4.2
SILC(Bip)	Bipy	[bmim][PF ₆]	[bmim][PF ₆]	4.0	3.0
SILC(Bih)	[BIHB]Br ₂	[bmim][PF ₆]	[bmim][PF ₆]	3.9	3.7
SC(Bip)	Bipy	H ₂ O	-	3.2	-
SC(Bih)	[BIHB]Br ₂	H ₂ O	-	2.0	-

^a Percentage expressed per mass of CNFs.

^b Percentage express per total mass of the catalyst.

Table 2. Adsorption and kinetic constants found for the reference catalyst and SILC(Bih). ^a					
Adsorption constants [L mol ⁻¹]			Kinetic constants [mol g _{Pd} ⁻¹ s ⁻¹]		
	Reference	SILC(Bih)		Reference	SILC(Bih)
K _Y	23.1	35.9	k ₁	2486.1	2503.3
K _N ^b	-	9.6	k ₂	1162.3	54.1
K _E	0.8	0.1	k ₃	208.8	154.4
K	8.3	4.7	k ₄	11.1	10.1
K _H ^c	1 10 ⁻³	2 10 ⁻³			

^a Reaction conditions: 4.1 g of 1-hexyne, 2.82 g of octane as internal standard, 0.3 g of catalyst, 303 K and 1.05 MPa of H₂ in 200 mL of n-heptane.

^b Dimensionless

^c This constant is the product K_{H2}C_{H2} and is dimensionless.

Table 3. Performance of the various catalysts tested in the hydrogenation of hexyne. ^a			
Catalyst	S ^b [%]	R [mol mol _{Pd} ⁻¹ s ⁻¹]	TOF [s ⁻¹]
Reference	88.0	47.0	223.8
SILC(Bip)	97.0	4.3	29.5
SILC(Bih)	94.0	11.0	60.8
SC(Bip)	98.4	1.7	11.5
SC(Bih)	97.8	1.4	7.6

^a Reaction conditions: 4.1 g of 1-hexyne, 2.82 g of octane as internal standard, 0.3 g of catalyst, 303 K and 1.05 MPa of H₂ in 200 mL of n-heptane.

^b Selectivity towards 1-hexene at 25% conversion

Table 4. Determination of 1-hexyne, 2-hexene, <i>n</i> -hexane and H ₂ solubility in [bmim][PF ₆], [C ₂ OHmim][BF ₄] and [C ₃ CNmim][Tf ₂ N] by ¹ H NMR spectroscopy.				
Ionic Liquid	Concentration [M]			
	1-hexyne	1-hexene	<i>n</i> -hexane	H ₂ [mM] ^a
[bmim][PF ₆]	1.24	0.23	0.07	0.97 ^b
[C ₃ CNmim][Tf ₂ N]	0.85	0.18	0.06	0.47
[C ₂ OHmim][BF ₄]	0.17	<0.01	0.06	1.28 ^c

^a measured at 10.1 MPa and adjusted for 0.101 MPa.

^b from ref [32].

^c from ref [29].

Table 5. Binding energies of Pd 3 5/2			
Catalyst	Pd 3d 5/2 (eV)		Reference
	Pd(0)	Pd(II)	
Reference	335.4	337.2	
SC(Bip)	335.3	338.1	
SC(Bih)	335.2	337.9	
Pd(0)	335.4		[53]
PdO		337.1	[54]
PdCl ₂ (bipy)		338.1	[55]
Pd(C ₂ H ₃ O ₂) ₂		338.8	[56]

References

1. Bartholomew, C.H. and R.J. Farrauto, *Fundamentals of industrial catalytic processes*. 2nd ed. ed. 2006, Hoboken, New Jersey: Wiley-Interscience.
2. Blaser, H.-U., A. Indolese, A. Schnyder, H. Steiner, and M. Studer, *J. Mol. Catal. A* 173 (2001) p. 3-18.
3. Garcia-Mota, M., B. Bridier, J. Perez-Ramirez, and N. Lopez, *J. Catal.* 273 (2010) p. 92-102.
4. Mallat, T. and A. Baiker, *Appl. Catal. A* 200 (2000) p. 3-22.
5. Nijhuis, T.A., G. van Koten, F. Kaptejn, and J.A. Moulijn, *Catal. Today* 79-80 (2003) p. 315-321.
6. Schlogl, R., K. Noack, H. Zbinden, and A. Reller, *Helv. Chim. Acta* 70 (1987) p. 627-679.
7. Yu, J. and J.B. Spencer, *Chem. Comm.* (1998) p. 1103-1104.
8. Tschan, R., M.M. Schubert, A. Baiker, W. Bonrath, and H. Lansink-Rotgerink, *Catalysis Letters* 75 (2001) p. 31-36.
9. Schmid, G., S. Emde, V. Maihack, W. Meyer-Zaika, and S. Peschel, *Journal of Molecular Catalysis A: Chemical* 107 (1996) p. 95-104.
10. Schmid, G., M. Harms, J.O. Malm, J.O. Bovin, J. Van Ruitenbeck, H.W. Zandbergen, and W.T. Fu, *J. Am. Chem. Soc.* 115 (1993) p. 2046-2048.
11. Huang, J., T. Jiang, B.X. Han, H.X. Gao, Y.H. Chang, G.Y. Zhao, and W.Z. Wu, *Chem Commun* (2003) p. 1654-1655.
12. Molnar, A., A. Sarkany, and M. Varga, *J. Mol. Catal. A* 173 (2001) p. 185-221.
13. Sulman, E.M., *Rus. Chem. Rev.* 63 (1994) p. 923-936.
14. Boitiaux, J.P., J. Cosyns, and S. Vasudevan, *Applied Catalysis* 15 (1985) p. 317-326.

15. Rajaram, J., A.P.S. Narula, H.P.S. Chawla, and S. Dev, *Tetrahedron* 39 (1983) p. 2315-2322.
16. Green, B.E., C.S. Sass, L.T. Germinario, P.S. Wehner, and B.L. Gustafson, *J. Catal.* 140 (1993) p. 406-417.
17. Aramendia, M.A., V. Borau, C. Jimenez, J.M. Marinas, M.E. Sempere, and F.J. Urbano, *Applied Catalysis* 63 (1990) p. 375-389.
18. Bronstein, L.M., D.M. Chernyshov, I.O. Volkov, M.G. Ezernitskaya, P.M. Valetsky, V.G. Matveeva, and E.M. Sulman, *J. Catal.* 196 (2000) p. 302-314.
19. Sulman, E., Y. Bodrova, V. Matveeva, N. Semagina, L. Cervený, V. Kurtc, L. Bronstein, O. Platonova, and P. Valetsky, *Applied Catalysis A: General* 176 (1999) p. 75-81.
20. Semagina, N., A. Bykov, E. Sulman, V. Matveeva, S. Sidorov, L. Dubrovina, P. Valetsky, O. Kiselyova, A. Khokhlov, B. Stein, and L. Bronstein, *J. Mol. Cat. A* 208 (2004) p. 273-284.
21. Schmid, G., *Chemical Reviews* 92 (1992) p. 1709-1727.
22. Léger, B., A. Denicourt-Nowicki, H. Olivier-Bourbigou, and A. Roucoux, *Tetrahedron Letters* 50 (2009) p. 6531-6533.
23. Hu, Y., Y.Y. Yu, Z.S. Hou, H. Li, X.G. Zhao, and B. Feng, *Adv. Synth. Catal.* 350 (2008) p. 2077-2085.
24. Hu, Y., H.M. Yang, Y.C. Zhang, Z.S. Hou, X.R. Wang, Y.X. Qiao, H. Li, B. Feng, and Q.F. Huang, *Catal. Commun.* 10 (2009) p. 1903-1907.
25. Tribolet, P. and L. Kiwi-Minsker, *Catal. Today* 105 (2005) p. 337-343.
26. Tribolet, P. and L. Kiwi-Minsker, *Catal. Today* 102-103 (2005) p. 15-22.
27. Terasaki, N., T. Akiyama, and S. Yamada, *Chem. Lett.* (2000) p. 668-669.
28. Dupont, J., C.S. Consorti, P.A.Z. Suarez, and R.F.d. Sousa, *Org. Synth.* 79 (2004) p. 236.

29. Yang, X., N. Yan, Z.F. Fei, R.M. Crespo-Quesada, G. Laurency, L. Kiwi-Minsker, Y. Kou, Y.D. Li, and P.J. Dyson, *Inorg. Chem.* 47 (2008) p. 7444-7446.
30. Cui, Y.G., I. Biondi, M. Chaubey, X. Yang, Z.F. Fei, R. Scopelliti, C.G. Hartinger, Y.D. Li, C. Chiappe, and P.J. Dyson, *Phys. Chem. Chem. Phys.* 12 (2010) p. 1834-1841.
31. Zhao, D.B., Z.F. Fei, R. Scopelliti, and P.J. Dyson, *Inorg. Chem.* 43 (2004) p. 2197-2205.
32. Dyson, P.J., G. Laurency, C.A. Ohlin, J. Vallance, and T. Welton, *Chem Commun* (2003) p. 2418-2419.
33. Singh, U.K. and M. Albert Vannice, *J. Catal.* 191 (2000) p. 165-180.
34. Macey, R.I. and G.F. Oster, *Berkeley Madonna™* (1997-2001) p.
35. Rosenbrock, H.H. and C. Storey, *Computational Techniques for Chemical Engineers*. 1966, Oxford: Pergamon Press.
36. Crespo-Quesada, M., M. Grasemann, N. Semagina, A. Renken, and L. Kiwi-Minsker, *Catal. Today* 147 (2009) p. 247-254.
37. Semagina, N., M. Grasemann, N. Xanthopoulos, A. Renken, and L. Kiwi-Minsker, *J. Catal.* 251 (2007) p. 213-222.
38. Bruehwiler, A., N. Semagina, M. Grasemann, A. Renken, L. Kiwi-Minsker, A. Saaler, H. Lehmann, W. Bonrath, and F. Roessler, *Ind. Eng. Chem. Res.* 47 (2008) p. 6862-6869.
39. Lindlar, H., *Helvetica Chimica Acta XXXV, Fasciculus II* (1952) p. 446-450.
40. Schlogl, R., K. Noack, H. Zbinden, and A. Reller, *Helvetica Chimica Acta* 70 (1987) p. 627-679.
41. Mikkola, J.P., P. Virtanen, H. Karhu, T. Salmi, and D.Y. Murzin, *Green Chem.* 8 (2006) p. 197-205.
42. Mikkola, J.P.T., P.P. Virtanen, K. Kordas, H. Karhu, and T.O. Salmi, *Applied Catalysis a-General* 328 (2007) p. 68-76.

43. Ruta, M., G. Laurency, P.J. Dyson, and L. Kiwi-Minsker, *The Journal of Physical Chemistry C* 112 (2008) p. 17814-17819.
44. Yan, N., X. Yang, Z.F. Fei, Y.D. Li, Y. Kou, and P.J. Dyson, *Organometallics* 28 (2009) p. 937-939.
45. Zhou, L. and L. Wang, *Synthesis-Stuttgart* (2006) p. 2653-2658.
46. Somorjai, G.A., *Science* 227 (1985) p. 902-908.
47. Boehm, H.P., *Carbon* 40 (2002) p. 145-149.
48. Biniak, S., G. Szymanski, J. Siedlewski, and A. Swiatkowski, *Carbon* 35 (1997) p. 1799-1810.
49. Yue, Z.R., W. Jiang, L. Wang, S.D. Gardner, and C.U. Pittman, *Carbon* 37 (1999) p. 1785-1796.
50. Besson, M. and P. Gallezot, *Catal. Today* 81 (2003) p. 547-559.
51. Panpranot, J., O. Tangjitwattakorn, P. Praserttham, and J.G. Goodwin Jr, *Applied Catalysis A: General* 292 (2005) p. 322-327.
52. Ulan, J.G. and W.F. Maier, *J. Mol. Catal.* 54 (1989) p. 243-261.
53. Johansson, G., J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.* 2 (1973) p. 295-317.
54. Fleisch, T.H. and G.J. Mains, *J. Phys. Chem.* 90 (1986) p. 5317-5320.
55. Nefedov, V.I., Zakharov.Ia, Moiseev, II, Poraikos.Ma, Vargafti.Mn, and A.P. Belov, *Zh. Neorg. Khim.* 18 (1973) p. 3264-3268.
56. Nefedov, V.I., Y.V. Salyn, Moiseev, II, A.P. Sadovskii, A.S. Berenbljum, A.G. Knizhnik, and S.L. Mund, *Inorg. Chim. Acta* 35 (1979) p. L343-L344.