









**Figure 3: Binding energies in X-ray photoelectron analyses: (A) Pd/SiO<sub>2</sub> and (B) Pd/SiO<sub>2</sub>-ODPA.**

Figure 3 described XPS results for (A) the bare and (B) the tethered Pd/SiO<sub>2</sub> catalysts. The calibration of binding energy was referenced to the C 2p peak at 285 eV. All deconvolution peaks fitted by Gaussian functions after deleting Shirley-background. The binding energy (BE) peaks of 335 eV and 340 eV were assigned to 3d<sub>5/2</sub> and 3d<sub>3/2</sub> of metallic palladium (Pd (0)). Correspondingly, the other deconvoluted BE peaks were observed at first pair of 337 eV and 342 eV (Pd (II), PdO) and the next pair of 338 eV and 343 eV (Pd (IV), PdO<sub>2</sub>). These deconvoluted peaks areas for the Pd/SiO<sub>2</sub> were decided to 45%: Pd (0), 30%: Pd (II), and 25%: Pd (IV), respectively. Subsequently, those for the Pd/SiO<sub>2</sub>-ODPA were calculated to 53%: Pd (0), 30%: Pd (II), and 18%: Pd (IV). These results indicate the zero-valent metal species on the surface increased after the surface modification using organophosphonic acid. The increased metallic Pd (0) component might assist to promote the HDC reactivity. In summary, the high HDC performance for the tethered Pd/SiO<sub>2</sub>-ODPA catalyst stems from [1] its surface affinity gathering hydrophobic chlorobenzene, and [2] high concentration of the zero-valent Pd (0) on the Pd particle surface.

**Acknowledgements:** This research was supported from Grant-in-Aid for “H28 applied and scientific research (A) of the CST” in Nihon University. I appreciate Dr. Tetsushi Umegaki for his help of the XPS measurement.

#### References:

- Díaz E., Casas J. A., Mohedano Á. et al. (2009); *Ind. Eng. Chem. Res.* 48 (7): 3351-3358
- Kitanosono T., Zhu L., Liu C., Xu P., Kobayashi S (2015); *J. Am. Chem. Soc.* 137 (49): 15422-15425
- Kitanosono T., Xu P., Isshiki S., Zhu L., Kobayashi, S., et al. (2014); *Chem. Commun.* 50 (66): 9336-9339
- Leung F. K.-C., Ishiwari F., Shoji Y., Nishikawa T., et al. (2017); *ACS Omega* 2 (5):1930- 1937
- Yamada Y. M. A., Ohno A., Sato T., Uozumi Y. (2015); *Chem. Eur. J.* 21 (48): 17269-17273
- Dong Z., Le X., Liu Y., Dong C., Ma J. (2014); *J. Mater. Chem. A* 2 (44): 18775-18785
- Dong Z., Le X., Dong C., Zhang W., Li X., Ma J. (2015); *Appl. Catal. B Environ.* 162: 372-380
- Hara T., Mori K., Oshiba M., Mizugaki T., et al. (2004); *Green Chem.* 6 (10): 507-509
- Hara T., Kaneta T., Mori K., Mitsudome T., et al. (2007); *Green Chem.* 9 (11): 1246-1251
- Navon R., Eldad S., Mackenzie K. et al. (2012); *Appl. Catal. B: Environ.* 119-120: 241-247
- Uozumi Y., Yamada Y. M. A. (2009); *The Chem. Rec.* 9, 51-65
- Yoneda T., Aoyama T., Takido T., Konuma K. (2013); *Appl. Catal. B: Environ.* 142-143, 344-353
- Yoneda T., Aoyama T., Koizumi K., Takido T. (2014); *Chem. Lett.* 43(10): 1603-1606
- Yoneda T. (2016); *Organohalogen Compounds* 78: 1050-1052
- Silverman B. M., Wieghaus K. A., Schwartz J. (2005); *Langmuir* 21 (1): 225-228
- Dubey M., Weidner T., Gamble L. J., Castner D. G. (2010); *Langmuir* 26 (18): 14747-14754
- Vega A., Thissen P., Chabal, Y. J. (2012); *Langmuir*, 28 (21): 8046-8051
- Hanson E. L., Schwartz J., Nickel B. et al. (2003); *J. Am. Chem. Soc.*, 125 (51): 16074-16080
- Hsu C.-W., Liou H.-R., Su, W.-F., Wang (2008); *L. J. Colloid. Interface Sci.* 324 (1-2): 236-239