

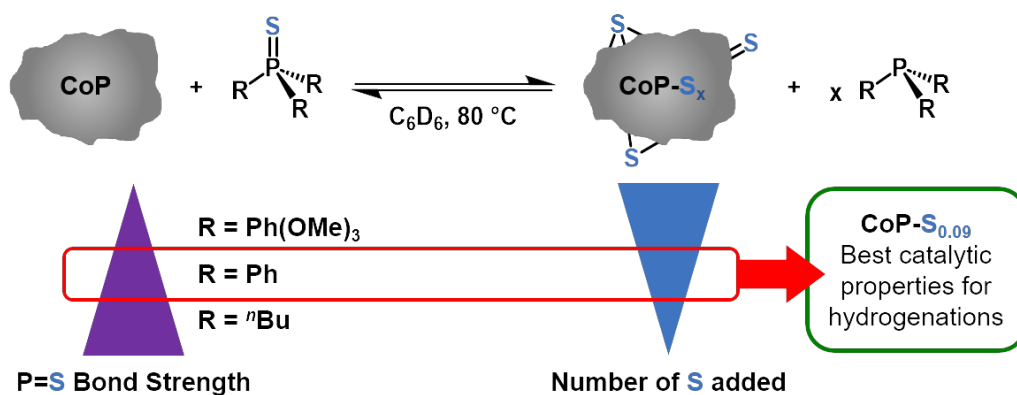
Controlled Modification of Cobalt Phosphide by Sulfur for Tuned Catalytic Properties in Hydrogenation

N. A. Arnosti¹, V. Wyss¹, M. F. Delley^{1*}

¹University of Basel, St. Johannis-Ring 19, 4056 Basel

Transition metal phosphides have shown promise as alternatives to the typical noble-metal based catalysts of water splitting and hydrotreating applications.¹⁻² A small amount of sulfur incorporated into the transition metal phosphide has been shown to significantly improve their catalytic performance.³⁻⁵ This sulfur effect is not well understood. This is in part because conventional synthesis methods of sulfur-doped phosphides typically result in a wide distribution of chemical environments for sulfur both inside and on the surface of the phosphide, which is challenging to analyze.⁴⁻⁵

Here, we present a novel approach to modify transition metal phosphides with sulfur. We used phosphine sulfides (SPR_3) as molecular reagents to transfer sulfur to cobalt phosphide (**CoP**). This enabled the addition of controlled amounts of sulfur to the surface of **CoP**. Furthermore, variation of the P=S bond strength of the SPR_3 reagents revealed that there is a distribution of different S-sites on the surface of **CoP** with a range of surface binding strengths between 69 and 84 kcal/mol. We probed the effect of different amounts and types of sulfur on **CoP** on its catalytic performance in the hydrogenation of α,β -unsaturated aldehydes. Our results suggest that an intermediate amount of sulfur on **CoP** leads to the best catalytic performance. The fundamental information about the surface chemistry of **CoP** and its relationship with catalytic properties found herein shows important new routes for catalyst design.



- Oyama S. Ted, Gott Travis, Zhao Haiyan, Lee Yong-Kul, *Catal. Today* **2009**, *143*, 94-107.
- Shi Yanmei, Zhang Bin, *Chem. Soc. Rev.* **2016**, *45*, 1529-1541.
- Bando Kyoko K., Wada Takahiro, Miyamoto Takeshi, Miyazaki Kotaro, Takakusagi Satoru, Koike Yuichiro, Inada Yasuhiro, Nomura Masaharu, Yamaguchi Aritomo, Gott Travis, Oyama S. Ted, Asakura, Kiyotaka, *Catal.* **2012**, *286*, 165-171.
- Cabán-Acevedo Miguel, Stone Michael L., Schmidt J. R., Thomas Joseph G., Ding Qi, Chang Hung-Chih, Tsai Meng-Lin, He Jr-Hau, Jin Song, *Nat. Mater.* **2015**, *14*, 1245-1251.
- Kibsgaard Jakob, Jaramillo, Thomas F., *Angew. Chem. Int. Ed.* **2014**, *53*, 14433-14437.