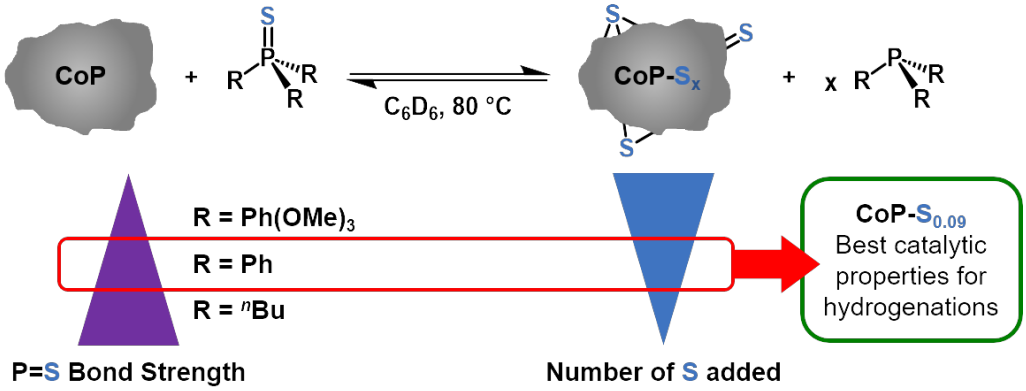
Controlled Modification of Cobalt Phosphide by Sulfur for Tuned Catalytic Properties in Hydrogenation

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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.



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