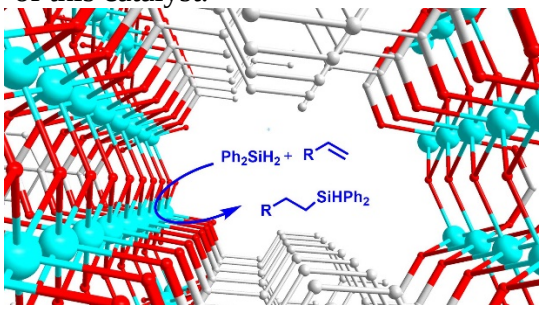
ALKENE HYDROSILYLATION CATALYZED BY EASILY ASSEMBLED Ni(II)-CARBOXYLATE MOFs

Zhikun Zhang, Lichen Bai and Xile Hu*

Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), ISIC-LSCI, Lausanne 1015, Switzerland, xile.hu@epfl.ch

Catalytic hydrosilylation of alkenes is one of the most important methods to synthesize organosilanes, which are precursors to silicon-based polymers and intermediates in organic synthesis. Pt-based catalysts are most efficient for hydrosilylation. However, the low abundance and high cost of Pt have motivated the development of base metal catalysts.[1] Despite this progress, the multi-step synthesized ligands and air and moisture sensitive catalysts would limit their practical applications, especially in large-scale synthesis. More importantly, the separation of homogeneous catalysts from reaction mixture can be problematic and costly.

In industry, heterogeneous catalyst are desirable and popular because they are amenable to immobilization and separation, which can reduce the cost owing to repeated use of catalysts and convenient separation. However, base metal based heterogeneous catalysis for hydrosilylation of alkene still remains rare, especially the easily assembled heterogeneous catalysts. Heterogenized catalysts based on metal-organic frameworks (MOFs) exhibit both the tunability of homogeneous catalysts and the stability and practicality of heterogeneous catalysts.[2] Inspired by our interest in heterogeneous hydrosilylation of alkenes[3] and pioneering work[4], we reported the first Ni MOF catalysts[5] for *anti*-Markovnikov hydrosilylation of alkenes.[6] These catalysts are bench-stable and easily assembled from simple Ni salts and carboxylic acids. The best catalyst gives turnover numbers up to 9500 and is robust even after 10 recycling runs. The catalyst can be applied for the hydrosilylation of a wide range of alkenes, achieving good synthetic utility and functional group tolerance. Mechanistic study can prove the heterogeneous property of this catalyst.



[1] J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15.

[2] L. Zhu, X. Q. Liu, H. L. Jiang and L. B. Sun, *Chem. Rev.*, 2017, **117**, 8129.

[3] (a). I. Buslov, F. Song and X. Hu, *Angew. Chem. Int. Ed.*, 2016, **55**, 12295; (b). I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc and X. Hu, *Angew. Chem. Int. Ed.*, 2015, **54**, 14523.

[4] L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan, J. Liang, Z. Zhang, T. Zhang, L. Long, J. Sun and W. Lin, *Angew. Chem. Int. Ed.*, 2016, **55**, 4962.

[5] S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khattak, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao and Z. Tang, *Nat. Energy*, 2016, **1**, 16184.

[6] Z. Zhang, L. Bai and X. Hu. *Chemical Science* 2019, **10**, 3791.