Catalysis in Silico - Where are We?
Modeling Reactions at Transition Metal Complexes

Notker Rösch

Department Chemie and Catalysis Research Center, Technische Universität München, Garching 85747 (Germany)

Modeling reactions in heterogeneous catalysis is challenging because usually the active site is unknown and has to be explored before the actual mechanism can be studied. Single-site catalysis experiments, aiming at unraveling the catalytic cycle, are especially helpful to computational catalysis, i.e., DFT based modeling, due to the potentially accessible detailed information about the active site. Experimental work addressed the selectivity of the conversion of ethene (in a feed also containing H_2) to *n*-butene or ethane on site-isolated rhodium complexes supported in faujasite.[1,2] $[Rh(C_2H_4)_2]^+$ complexes were found to catalyze predominantly C–C coupling, whereas complexes with added CO would favor ethane formation.[2]

Modeling the chemistry proceeding on the complex $[Rh(C_2H_4)_2]^+$ lead to the surprising conclusion that the catalyst at work cannot have this composition because hydrogenation was the only outcome predicted.[3] Taking into account the experimental feed rich in ethene, we argue that the transient species $[Rh(C_2H_4)_3]^+$ is the true *active* species, at variance with the speculation in experiment.[4] An added CO ligand favorably binds between both ethene moieties, hindering the mechanism leading to C–C coupling.[5] We provide strong arguments based on DFT results that the *active* species is the intermediate Rh-acyl complex $[Rh(COCH_2CH_3)(C_2H_5)(C_2H_4)]^+$, generated in situ during the start-up phase of the reaction.[5] These two examples are highlighting the insight, catalysis in silico is able to provide.

1. Serna, P., Gates, B. C. *J. Am. Chem. Soc.* **2011**, *133*, 4714.
2. Martinez-Macias, C., Serna, P., Gates, B. C. ACS Catal. **2015**, *5*, 5647.
3. Govindasamy, A., Markova, V. K., Genest, A., Rösch, N. *Catal. Sci. Technol.* **2017**, *7*, 102.
4. Vummaleti, S. V. C., Kuriakose, N., Dinda, S., Wu, Y., Genest, A., Rösch, N. *Catal. Sci. Technol.* **2019**, 9, 2781.
5. Vummaleti, S.V.C., Genest, A., Kuriakose, N., Rösch, N. *ACS Catal.* **2018**, 8, 9836.