Modeling transformations catalyzed by a zeolite-supported Rh(I) complex

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Abstract: We present model density functional theory calculations on a zeolite-supported Rh(I) complex to rationalize the experimentally observed selectivities for a feed of H_2 and ethene. Our findings ruled out the well-characterized faujasite-supported complex $[Rh(C_2H_4)_2]^+$ as active species for ethene dimerization in an ethene rich feed. We propose an alternative active catalyst, formed *in situ* in the catalytic cycle. We also examined other reactions such as dehydration reactions of ethanol at a Rh(I) center anchored in a faujasite.

Keywords: Zeolite-supported Rh(I), selective C–C coupling, dehydration, QM/MM, ethylene

1. Introduction

Modeling reactions in heterogeneous catalysis is challenging because often the active site is unknown and has to be explored before the mechanism can be studied. Single-site catalysis experiments, aiming at unraveling the catalytic cycle, are especially helpful to computational catalysis, due to the potentially accessible detailed information about the active site. In our first example, experimental work addressed the selectivity of the conversion of ethene to *n*-butene or ethane on site-isolated rhodium complexes and small rhodium clusters, supported in faujasite.[1,2] Under ethene-rich conditions, $[Rh(C_2H_4)_2]^+$ complexes were reported to catalyze predominantly C–C coupling, whereas under hydrogen-rich conditions small Rh clusters are responsible for producing ethane. Modeling such selectivities is a tremendous challenge even with modern computational methods, as only small energy variations are involved. We also inspected the hypothetical reaction of dehydrating ethanol at a Rh(I) center anchored inside a faujasite. At variance to the pure zeolite we aimed at possible effects of metal sites in such reactions. This research turned out to require the synergy between quantum chemical and microkinetic modeling to provide a full understanding.

2. Theoretical

For modeling the selective C–C coupling as well as hydrogenation at the faujasite-supported Rh(I) center, we chose an 83T cluster model taken from the zeolite lattice, 278 atoms in total, for a molecular strategy and the full zeolite for a plane-wave based strategy. In the first, QM/MM based approach we used a QM partition of 5T centers that comprises an AlO_4 moiety carrying the metal complex, surrounded by 4 neighboring Si units. The electronic structure calculations were carried out with the software Gaussian 09 and 6-31G(d,p) basis sets for H, C, O, Al, and Si, as well as the Stuttgart–Dresden effective core potential MWB28 for Rh. The remainder of the 83T atoms, surrounding the QM zeolite partition, were assigned as low-level (MM) partition, described by the universal force field (UFF). The plane-wave calculations were carried out with the VASP package and we made sure that results from both approaches are comparable.[3] In all cases we applied the PBE exchange-correlation functional. We confirmed the nature of all stationary points by a normal mode analysis. In the following we present free energy values.

3. Results and discussion

Initially we followed the experimental suggestion and modeled the catalysis to be expected for the complex $[Rh(C_2H_4)_2]^+$ anchored in a faujasite.[4] We computed the mechanism when only the metal center is considered as active complex and also, when a bi-functional catalyst including a participation of the zeolite wall is assumed. For reactions at the metal center alone we determined a rather low barrier leading to ethane of only 33 kJ mol^{-1}. C–C coupling on the other hand was found to proceed over a barrier of 97 kJ mol^{-1}, substantially higher than that for hydrogenation, Figure 1. Given that the selectivity is at variance with the experiment, we searched for other active sites that could turn out to be the catalyst. A participation of the wall did not lower the barrier for C–C coupling, but rather increased it to ~130 kJ mol^{-1}. We also inspected Rh_3 and Rh_4 clusters, that were reported for experiments with a surplus of hydrogen. We showed that these clusters are extremely fast the activating hydrogen molecules and hence are covered in hydrogen. Therefore it is not surprising that for the selectivity of Rh_3 and Rh_4 clusters we determined very low barrier towards ethane formation, as found in experiment.[5,6] Finally we will present an alternative catalyst, that can be generated *in situ*, which blocks the possibility of ethylene hydrogenation and hence is active for C–C coupling with a barrier of ~83 kJ mol^{-1}.

For the conversion of ethanol to either ethylene or acetaldehyde we show the importance of microkinetic modeling. It turned out, that the selectivity is extremely sensitive to the amount of reactant molecules and the reaction temperature as both influence how many ligands the Rh(I) complex carries.[7]

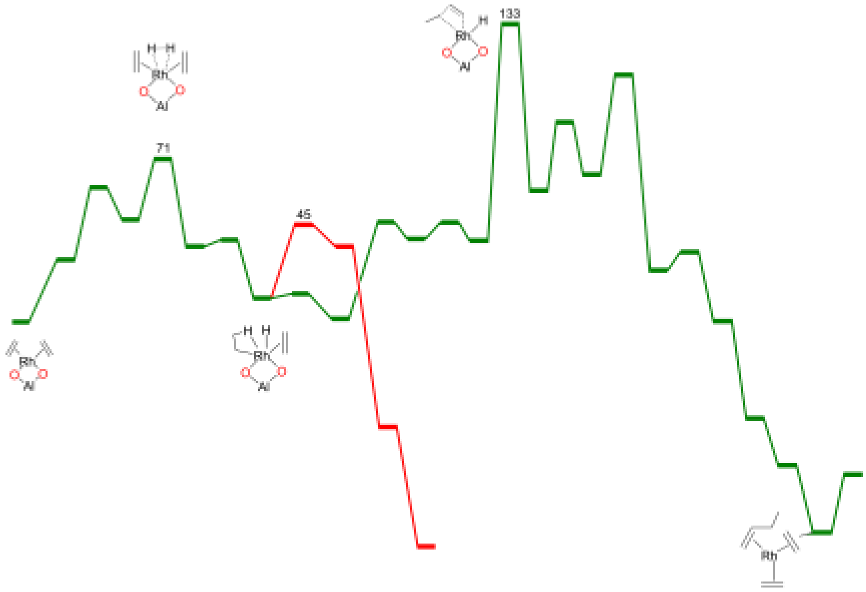

Figure 1. Potential energy profile for the $[Rh(C_2H_4)_2]^+$ complex. Green – C–C coupling, red – hydrogenation.

4. Conclusions

We modeled C–C coupling, hydrogenation and dehydration reactions at a zeolite-supported Rh complex. We show in all cases that a detailed account for the environment of the catalyst is crucial to a successful modeling. This enabled us to trace the *in situ* formed catalyst species active in C–C coupling. In a similar fashion the selectivities for dehydration vs dehydrogenation can only be accounted for by including environment and temperature with the help of a microkinetic model.

References

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