Modeling heterogeneous catalysis is challenging because often the active site is unknown and has to be explored by computing the mechanism on each likely candidate. Single-site catalysis experiments, aiming at unraveling the catalytic cycle, are especially helpful in computational catalysis, due to the detailed information provided about the active site. Experimental work addressed the selectivity in the conversion of ethene to n-butene or ethane on site-isolated di-ethylene Rh(I) complexes and small rhodium clusters, supported in a channel of a faujasite. We examined computationally the mechanism and the selectivity of this system for the varying conditions. For small rhodium clusters, we determined with the help of a thermodynamic model that Rh₄ clusters will be catalytically active, while Rh₃ will quickly be covered by coke. With our computational catalysis study, we highlight how modeling can substantially contribute to the understanding of the catalytic mechanism at work, even in cases where detailed experimental information about the active site and extensive spectroscopic studies are available.