Teaching Fe to behave like Pd in Catalytic Bond Activation based on the Activation Strain Model

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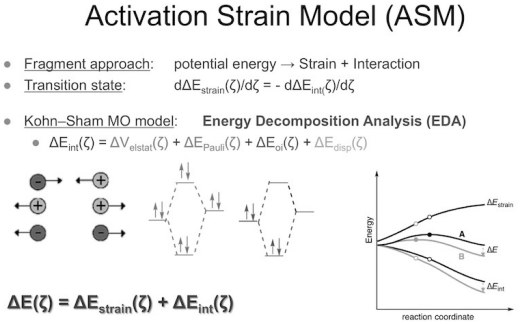
Abstract: A systematic approach for first-principle catalyst design is presented in which potential energy surface is obtained, followed by the activation strain analysis to study the steric and electronic effect separately and determine which is the key factor to influence the energy barrier. If the steric effect dictates the catalytic activity, the angle or other structural parameters can be frozen in the model reaction analysis to achieve the optimum structure. This can be achieved, for example, by using a bridging ligand. If the electronic effect is the focus of the tuning, which is indicated by the interaction energy term in the activation strain model[1,2], the problem can be tackled by adjusting the metal electronic structure to enhance the catalyst–substrate interaction via the choice of ligands with different electron-donating and accepting capability. Thus, based on this approach, we tried to develop a new type of iron-based catalysts that mimic the behavior of palladium catalysts in cross-coupling reactions. Firstly, we have investigated the activity of the model catalyst complexes $Fe(CO)_4$ toward CH_3X (with X = H, Cl, CH_3) C-X oxidative addition, including different charges and spin states. Secondly, such different reactivity between $Fe(CO)_4$ and Pd in activating these model reactions are compared and reasons can be explained by electronic-structure and activation strain analysis. Finally, by applying the aforementioned approach the behavior of palladium can be mimic by iron complex. Our long-term purpose is to find ways to replace palladium for bond activation and cross-coupling reactions.



References

1) L. P. Wolters, F. M. Bickelhaupt, *WIRES Comput. Mol. Sci.* **2015**, *5*, 324

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