

## A Combined Static and Dynamic Density Functional Theory Approach to Elementary Reaction Steps in Homogeneous Catalysis.

Peter Margl, Tom K. Woo, Rochus Schmid, Liqun Deng and Tom Ziegler\*

Department of Chemistry, University of Calgary, 2500 University Drive, N.W., Calgary, Alberta, T2N 1N4, CANADA

email: ziegler@ucalgary.ca

Phone: (voice) 403 220-5368 (fax) 403 289-9488

**KEYWORDS:** molecular modeling, density functional theory, QM/MM, Brookhart catalyst, constrained geometry catalyst, *ab initio* molecular dynamics

### ABSTRACT

We describe an approach in which first principle molecular dynamics calculations based on density functional theory (DFT) are used to locate reaction pathways and estimate free energies of activation whereas static DFT calculations were used to obtain stationary points and relative energies as well as reaction paths by the intrinsic reaction coordinate method. The approach has been applied to (a) copolymerization of polar and non-polar monomers by nickel and palladium based catalysts as well as (b) a comparison between rhodium and iridium based catalysts in Monsanto's acetic acid process (c) carbonylation of methane by a rhodium catalyst.

### Introduction

Homogenous catalytic systems have often been used to model more complicated heterogeneous systems. However, even seemingly simple homogenous systems pose many challenges for computational chemists. Often times a first principle's calculation involves a stripped down model that only vaguely resembles the true system. If large, bulky ligand systems are involved they are most often neglected in high level calculations with the hope that they do not substantially influence the nature of the reaction mechanisms. Unfortunately, the surrounding ligand system or matrix can often play a crucial mechanistic role. In addressing this issue, the combined quantum mechanical/molecular mechanics (QM/MM) method<sup>1</sup> has recently received significant attention. In this hybrid method part of the molecule, such as the active site, is treated quantum mechanically while the remainder of the system is treated with a molecular mechanics force field. This allows extremely large systems which are out of the reach of pure QM calculations to be studied in an efficient and detailed manner. We have applied the QM/MM method to study the homogenous Brookhart diimine Ni olefin polymerization catalyst.<sup>2</sup> Since the QM/MM method was originally conceived to more adequately treat larger, more "real life" systems it naturally has applications in the area of heterogeneous catalysts.

Recently, our group has been utilizing Car-Parinello<sup>3</sup> flavor *ab initio* molecular dynamics to explore potential energy surfaces and to obtain free energy barriers for catalytic processes. We have determined free energy barriers for several processes at the *ab initio* molecular dynamics level for the Ti mono-Cp constrained geometry olefin polymerization catalysts, (CpSiH<sub>2</sub>NH)Ti-R<sup>+</sup>.<sup>4</sup> The results compare well with similar free energy barriers determined from more traditional "static" electronic structure calculations. We will demonstrate that the *ab initio* molecular dynamics method (i) provides a general way of determining finite temperature free energy barriers which are in good agreement with static methods, (ii) can be used to efficiently explore complicated free energy surfaces and (iii) that the method can be effectively utilized in a synergistic fashion with traditional static methods.

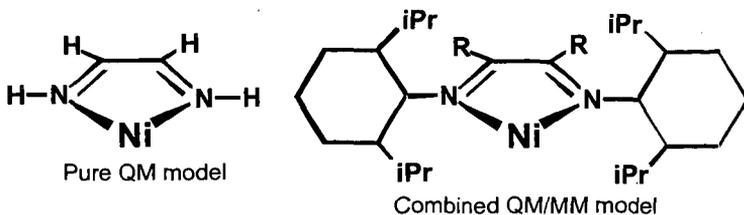
### Computational Details

The reported "static" density functional calculations were all carried out by the ADF program system, developed by Baerends and others.<sup>5</sup> Energy differences were calculated by including the local exchange-correlation potential by Vosko<sup>6</sup> *et al.* with Becke's<sup>7</sup> nonlocal exchange corrections and Perdew's<sup>8</sup> nonlocal correlation correction. For the QM/MM calculations a version of the ADF program system as modified according to Morokuma and co-workers was utilized with the AMBER<sup>9</sup> force field. For more details of the QM/MM work see reference<sup>10</sup>. All reported molecular dynamics simulations were carried out with the Car-Parinello Projector Augmented Wave (CP-PAW) code developed by Blöchl.<sup>11</sup> For more details of the molecular dynamics simulations and the constrained geometry work see references<sup>12</sup>.

### Results and Discussion

**Combined QM/MM:** Recently, Ni(II) and Pd(II) diimine based single-site catalysts have emerged as promising alternatives to newly developed metallocene catalysts for olefin polymerization.<sup>2</sup> Brookhart's group has shown that these catalyst are able to convert ethylene into high molecular mass polymers with a controlled level of polymer branching when bulky ligand systems are used.

We have investigated the chain propagation, chain termination and the chain branching processes with a truncated pure quantum mechanical model system where the bulky ligands are neglected and with a combined QM/MM model where the bulky ligands are included via a MM force field. Scheme 2 depicts the two model systems. The QM region of the QM/MM model is the same as the pure QM model.



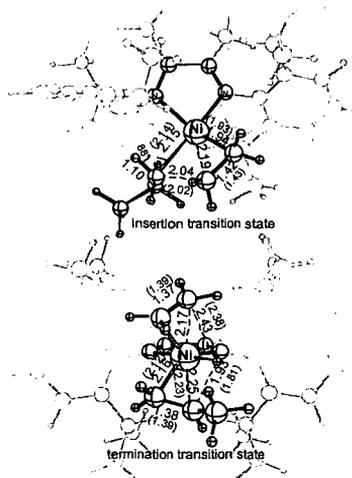
**Scheme 1**

Experimentally, it has been determined that the relative magnitude of the barriers are in the order insertion > isomerization > termination. Table 1 shows that the pure QM model does not reproduce this trend. In fact, the results of the pure QM simulation suggest that the catalyst should not produce polymers at all but rather dimers or oligomers.

Table 1.

process	Reaction Barrier, $\Delta H^\ddagger$ (kJ/mol)	
	pure QM model	QM/MM model
propagation	71	49
branching	52	64
termination	42	77

However, when bulky ligands are not neglected but rather modeled by molecular mechanics force field, the barriers do follow the experimentally established trends. Moreover, the calculated propagation barrier is in remarkable agreement with the experimental estimate of 40-46 kJ/mol.<sup>13</sup>



**Figure 1.** Combined QM/MM transition states for the propagation and termination processes. The parenthetical parameters are those of the equivalent pure QM transition states. The ghosted portions of the molecules represent the pure MM atoms.

**Ab Initio Molecular Dynamics:** We have examined several chain termination and long chain branching mechanisms with conventional "static" electronic structure calculations and with *ab initio* molecular dynamics in the density functional theory framework. Free energy barriers were computed by both methods and were found to be in excellent agreement with one another. Movies of all molecular dynamics simulations presented here can be found at our research group's world wide web home page <<http://www.chem.ucalgary.ca/groups/ziegler>>.

