Computational Chemistry

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Prediction of Rate Constants for Catalytic Reactions with Chemical Accuracy

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Computational chemistry now contributes to all areas of the chemical sciences and is widely used to guide the interpretation of experiments. In many applications, the information provided is only semiquantitative, providing models and trends that illuminate and assist the interpretation of experiments. But as the field moves increasingly towards prediction as well as interpretation, there is a growing need for reliable quantitative modelling, that is, for chemical accuracy. In some cases, this aim can be achieved. Structures of molecules and solids may be calculated with a high degree of accuracy; indeed, such calculations are now becoming routine. The calculation of accurate bond and reaction energies is less straightforward but can be achieved. Electronic structure, including band structures of solids, again poses challenges, but there is a growing number of reported examples of successful quantitative calculations. Reaction rates, however, have presented major difficulties. With high-level quantum mechanical calculations, accurate rates have been calculated for reactions involving small molecules, and there is considerable progress in the field of enzymatic reactions. But can chemical accuracy be achieved in reactions involving solids? This need is unquestionably one of the greatest challenges in contemporary computational materials and catalytic chemistry.

The recent article of Piccini et al.[1] represents a direct response to this challenge. The work focuses on reactions within microporous zeolite catalysts, which continue to receive widespread attention because of both their industrial importance and the fundamental scientific challenges posed by understanding catalytic processes and mechanisms within these materials. Computational techniques have contributed to and illuminated many aspects of zeolite science for over 30 years, as recently reviewed by van Speybroeck et al.[2] Modelling of microporous structures is now accurate and predictive;[3] simulation of sorption and diffusion has enjoyed wide success, and calculated diffusion coefficients are now beginning to achieve closer agreement with experiment.[4] There have been many successful studies of reaction mechanisms within zeolites, as discussed in Ref. [2], and the recent work of De Wispelaere et al.[5] illustrates the power of the metadynamics approach in modelling mechanisms. But the calculation of rates of reactions within zeolites has remained elusive. Transition-state theory (TST) requires highly accurate enthalpies and pre-exponential factors if the required degree of accuracy is to be achieved. Achieving accuracy in the calculation of these key parameters is notoriously difficult even for relatively simple processes, but for reactions in zeolites, it is even more demanding. The widely and successfully used approaches based on density functional theory (DFT) will, depending on the functional used, yield errors in activation energies of 10–20 $\mathrm{kJ\,mole^{-1}}$ (or more), and errors of this magnitude within a TST approach will result in rates that fail to meet the criterium of chemical accuracy (generally defined as within 4 $\mathrm{kJ\,mole^{-1}}$ deviation).

Piccini et al. tackle this problem through a carefully constructed multistage "divide and conquer" approach, in which the level of the calculations is increased step by step to achieve the required degree of accuracy, while using feasible amounts of computational resources. They consider reactions of methanol with ethene, propene and *trans*-2-butene, which are processes of real catalytic interest and importance for which accurate experimental data are available. They start with a standard and routine DFT approach to model the periodic zeolite; they then focus on the reaction site illustrated in Figure 1. A key feature of their method and one that has been widely used in other areas of solid-state science and in biomolecular modelling, is that the cluster is treated quantum mechanically and is embedded in a simpler, interatomic potential (or molecular mechanics) treatment of the surrounding lattice—a procedure often referred to as the quantum mechanics/molecular mechanics (QM/MM) approach. This region is modelled at a much higher level using perturbation theory (MP2) methods. Finally, to check the accuracy of the MP2 calculation, they focus on a small central region of the site and treat it at the highest level using couple cluster (CCI) theory. This stepwise approach allows them to achieve (and check) the accuracy of their calculations, while using realistic models with accessible computer resources. To calculate the pre-exponential factors, vibrational frequencies must be calculated, for which the DFT potential energy surface is adequate, provided that care is taken to include anharmonic terms.

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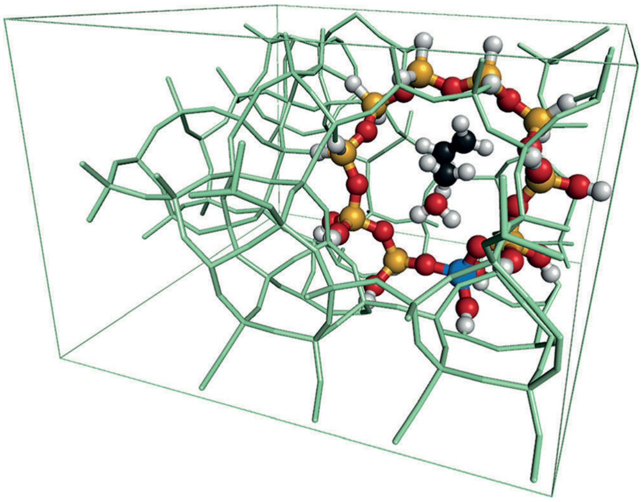

Figure 1. The embedded cluster used in the QM/MM calculations. The cluster treated at the high quantum mechanical level is highlighted. (figure reproduced from Ref. [1]).

The theoretical and computational approach leads to predicted rate constants that can then be compared with experimental values. The results are remarkable. Activation enthalpies were obtained that achieve the goal of chemical accuracy; they fall within 4 kJ mole^{-1} of the experimental values. The even more challenging calculation of reaction rates was again achieved with impressive accuracy. The experimental data are uncertain within a factor of ten and the calculated values are within a factor of 3 to 8 of observation. Chemical accuracy has thus been achieved for both enthalpies and reaction rates.

The procedures developed in this seminal study are far from routine. The multistep approach is an exacting method and the computational resources required are substantial. The implications of the work are, however, considerable. Chemical accuracy has been achieved for real and significant catalytic processes. We now have procedures that will enable the calculation of reaction rates for heterogeneously catalyzed reactions within experimental error. Accurate predictions of the variations of rates within active-site structures will be possible, and the coupling between modelling and experimental approaches will become even closer. Zeolites have the advantage that in many cases we have good knowledge of the active-site structure, which is far less well defined in many oxide and oxide-supported metal catalysts. But computational modelling has now reached the stage where it can provide reliable and quantitative rates of catalytic reactions, and this achievement is a very significant milestone in the field.

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