Heterogeneous Catalysis at the Molecular Level

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Heterogeneous catalysts provide efficient processes to produce many of the chemicals we take for granted in our everyday lives. By reducing the energy barrier to difficult chemical transformations they both reduce the time required for reactions and the size of chemical plants required. The reduced energy requirements for a catalysed reaction also allow us to obtain the desired product with less environmental impact than would be incurred using only non-catalysed reactions. This latter point is becoming ever more important with new catalysts which can improve product selectivity and play a role in green technologies continually in demand.

To obtain new catalysts we need as much information as possible on the operation of existing materials and an ability to find out what will happen if the catalyst structure or composition is altered. Even for a comparatively simple reaction such as the hydrogenation of acetone to propan-2-ol, the complexity of the surface reaction can be difficult to understand without the aid of computer simulation at the atomic level. The basic mechanism can be adapted from the Horiuti-Polanyi scheme for ethene hydrogenation over Pt group metals shown in Figure 1. Hydrogen adsorbs and dissociates on Pt surfaces to give atomically adsorbed hydrogen. From surface science temperature programmed desorption (TPD) measurements and vibrational spectroscopy acetone is thought to adsorb molecularly[1]. Surface hydrogen can then add across the C=O double bond to produce the

secondary alcohol, propan-2-ol. The alcohol has a much lower affinity for the surface than the ketone and so readily desorbs and is detected as product.

The first thing to note about this type of scheme is that the detailed structure of the surface is rather limited; it is a place where the reactants congregate, are activated and react. However, this reaction will not occur in the gas phase at any appreciable rate without the presence of the catalyst and so the surface itself must be more actively involved than this picture suggests. Computer simulation at the atomic scale is now able to provide this more detailed picture and allow us to review experimental data in the light of calculations.

To tackle these sort of processes we need to be able to describe the bond forming and breaking processes taking place and so some level of quantum mechanical treatment of the electronic states of the system is required. We have chosen periodic DFT with a planewave basis set and gradient corrected functionals (PW91) as implemented in the VASP program[2]. In earlier calculations it has been shown that this approach is able to give a good description of the H_2 dissociation process on Pt group metals[3] and with the additional computer power available from Newton and HPCx we have now been able to study the ketone adsorption[4].
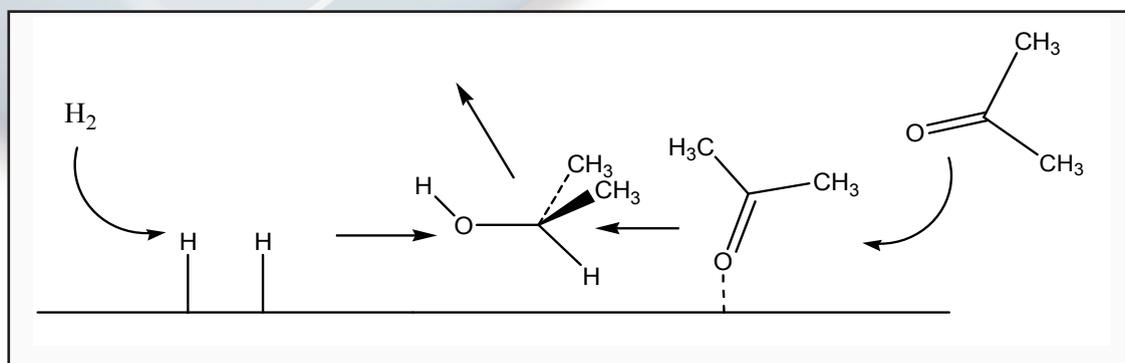
Figure 1: The Horiuti-Polanyi scheme adapted for ketone hydrogenation.
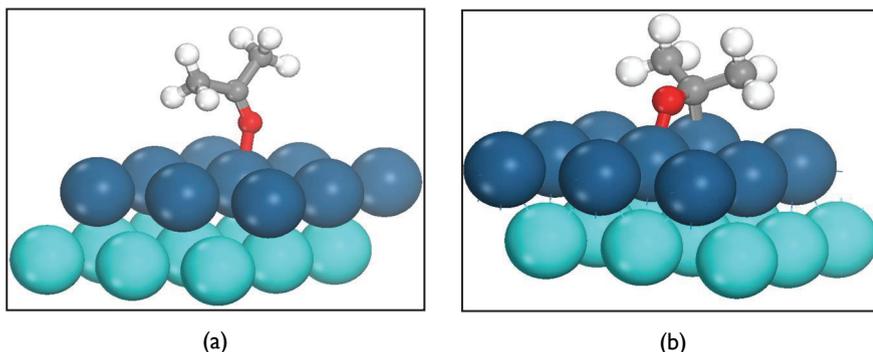
Figure 2: Optimised structures for acetone keto-isomer adsorbed on Pt(111). (a) end-on, and (b) side-on. Only two layers of the three layer simulation slab are shown.

Experimental TPD data and vibrational spectroscopy[1] suggested that two species are present on the Pt(111) surface; the end-on ketone (Figure 2a) which desorbs at 184 K and shows vibrational modes only weakly perturbed by interaction with the metal and a second species which desorbs at the higher temperature of 199 K and gives a lower vibrational frequency for the C=O stretch vibration between 1511 and 1610 cm⁻¹. This second species was assigned to acetone in a side-on adsorption mode (Figure 2b).

The structures in Figure 2 are actually from our optimisation calculations which showed that the side-on adsorption has a lower binding energy to the surface than the end-on mode (21 *cf* 40 kJ mol⁻¹). This can be understood in terms of the steric interaction of the acetone methyl groups with the surface which is greater in the side-on than in the end-on case. However this contradicts the experimental result since the lower binding energy should correspond to a lower desorption temperature.

Vibrational spectroscopy is one area in which simulation can make direct contact with experiment and so we also calculated the adsorbate vibrational modes for comparison with the experimental spectra. We were able to confirm the assignment of the low temperature peak as the end-on adsorbate with a calculated CO stretch frequency of 1600 cm⁻¹ which compared well with the experimentally reported value of 1640 cm⁻¹. However a calculation of the vibrational frequencies for the side-on adsorbate gave a C=O stretch of 1161 cm⁻¹. The lowering in frequency compared to the end-on form can be attributed to interaction with the surface, both O and C form bonds to Pt atoms and so the C=O bond itself is weakened. This also leads to the loss of planarity of the adsorbate as can clearly be seen in Figure 2b. So the side-on adsorption mode shows both

the wrong adsorption energy and vibrational data to be reconciled with experiment. This leaves the question of what surface species actually gives rise to the second signal observed in the experimental vibrational spectra?

To answer this we looked at isomerisation of the adsorbate. A molecule with C-H bonds adjacent to the C=O ketone group can undergo keto-enol isomerisation (Figure 3). In the gas phase the enol form of the molecule is only a tiny fraction of any given sample. Indeed we calculate an energy difference between the gas phase isomers of 50 kJ mol⁻¹. However
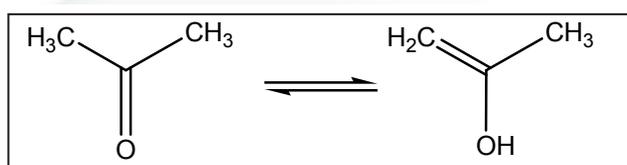
Figure 3: Isomers of acetone the ketone form (left) can undergo a proton transfer to give the enol (right).

the adsorption of the molecule to the surface lowers the energy of the system. This means that if the adsorption of the enol form to the surface is more favourable than the ketone by 50 kJ mol⁻¹ or more the balance could tip in its favour. Accordingly we studied the adsorption of enol and the de-protonated enolate forms of acetone on the surface. The most stable forms with energies quoted relative to gas phase ketone are shown in Figure 4. Both the enol and enolate are more favourable on the Pt surface than the end-on ketone form. In addition the enolate gives a C=O stretching frequency of 1574 cm⁻¹, within the experimental range for the mystery "species 2".
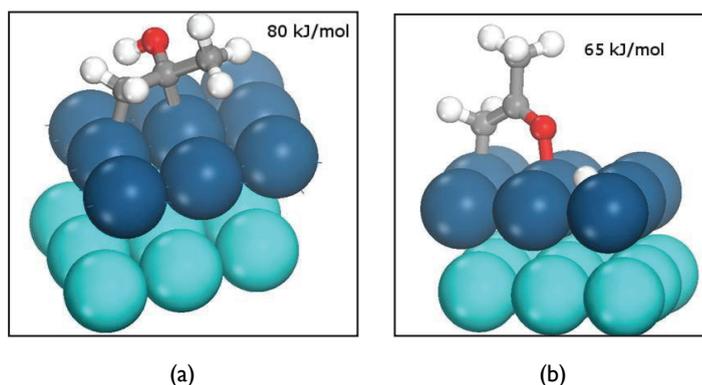
Figure 4: Optimised structures for (a) enol and (b) enolate with H adsorbed on Pt(111). Energies are quoted relative to the gas phase ketone with a positive value indicating favourable adsorption.

From these calculations we conclude that acetone adsorbing on a Pt surface will be present both as end-on and enol/enolate forms, *i.e.* the molecule will isomerise on the surface. This adds additional steps to the Horiuti-Polanyi scheme and suggests that hydrogenation may be across a C=C rather than a C=O double bond under conditions in which the isomerisation is faster than the hydrogenation of the ketone.

Most catalysts employ metal particles supported on oxides and so reactions may occur not only on the simple surfaces of the active metals but also at the interface between the oxide and metal particle. A case in point is the relatively new area of nano-particulate Au supported on various oxides. The particle size in this case is critical to the catalytic performance, bulk Au is inactive but particles on the nanometre scale have shown room temperature activity for the oxidation of CO to CO_2[5]. To study this chemistry the inclusion of the Au/oxide interface requires large unit cells to be constructed so that the periphery of the Au cluster can be included without interference between periodic images. To achieve this we are using the SIESTA[6] code to simulate a Au_{10} particle supported on a $Mg_{96}O_{96}$ supercell. One difference between this and periodic metal simulations of larger particles is that charge transfer between Au and the support oxide can significantly influence the electronic character of the metal particles. This is particularly important if the oxide surface is defective. Figure 5 shows the charge transfer from a surface oxygen vacancy to the Au_{10} cluster. This gives a cluster with an overall negative charge and we are currently investigating the effect this has on the adsorption and vibration of reactant molecules.

The calculations covered in this report require the consideration of many alternative positions on the surface for each isomer of a reactant. Each individual calculation of optimal adsorption geometry and vibrational frequencies are computationally intensive. The electron density for the metal surfaces is typically represented by a Fourier transform in the simulation cell requiring around 800,000 plane wave coefficients and the system sizes for the supported metal particles would have been impractical a few years ago. The large shared memory resources available on HPCx and Newton make such calculations possible on the required timescales. The accuracy of the calculations give us confidence to use the simulation results to help interpret experimental data from surface science experiments and are leading to an improved understanding of catalytic reaction mechanisms.
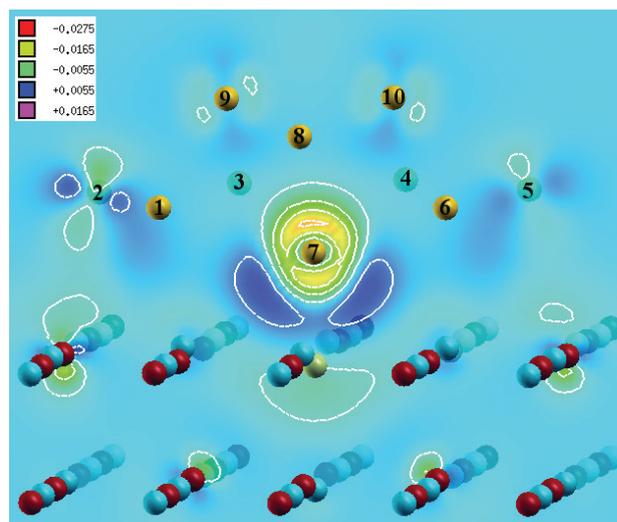
Figure 5: A Au_{10} cluster adsorbed at a surface oxygen defect on MgO(001) the contour plot shows the transfer of charge from the defect to the central Au atom of the cluster.

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