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The Reactivity of CO_2 and H_2 at Trapped Electron Sites at an Oxide Surface

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Abstract

We investigate the reactivity to H_2 of a chemisorbed CO_2 species at electron traps on oxide surfaces, taking the single electron F^+ oxygen vacancy of the MgO (100) terrace as a model system. We find that multiple hydrogen addition steps form three interacting catalytic cycles, leading to the evolution of formaldehyde, methanol or methane. Our results have general implications for the reactivity of CO_2 on metal oxides.

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Introduction

The recycling of CO_2 into a fuel or other useful products is a key challenge in contemporary chemistry. Recycling CO_2 to a hydrocarbon product could in principle give rise to a carbon-neutral energy storage process, with the added benefit that minimal changes to infrastructure would be needed to make use of whatever synthetic fuel is produced. The three main requirements for such a recycling process are: a method of capturing and storing CO_2, an efficient method of producing H_2 (without the consumption of fossil fuels, e.g. via photocatalytic water splitting), and finally, an efficient catalytic process allowing for the reaction of CO_2 with H_2 to give the desired fuel. Methanol is one of the most desirable synthetic hydrocarbon products due to its physical and chemical properties, which allow for ease of transportation and storage, and also the fact that it could be used for combustion directly as well as within a fuel cell. Additionally, dimethyl ether (DME) which is considered a promising replacement for diesel fuel, may be routinely produced by the dehydration of methanol.

Here, we determine the role of electrons trapped in oxygen vacancies for the reactiviy of CO_2 with H_2 as part of a methanol synthesis process. Specifically, we consider how the sites on an MgO (100) surface relate to those of the catalytic system Cu/ZnO/Al_2O_3, where oxygen vacancies of ZnO $[000\bar{1}]$ have been identified[1–5] as a potential active site.

We have focused on the F^+-centre, a 5-coordinate oxygen vacancy on the MgO terrace with a single electron localized at the defect. These vacancies are known to be rare, with defects at corners and edges having a much lower formation energy.[6,7] Of the accessible sites for surface chemistry, the terrace sites are expected to display the lowest reactivity due to the effect of the Madelung potential. It is therefore reasonable to assume that any reactivity seen here would be enhanced if the vacancies were to be found instead at edge and corner sites, making models of terrace defects an excellent "limiting case". Our previous work[8] found a stable chemisorbed configuration for CO_2 on a surface F^+-centre on MgO, and it is this model which we have taken as a starting point for a further study.

Although MgO may not be a suitable catalyst for the sort of conversion reaction described, our results have general implications for the role of electronic surface defects in the catalytic conversion of CO_2 into useful products. Specifically, a material with a strong tendency to trap electrons at an oxygen vacancy, but for which the formation and regeneration of those vacancies does not carry an excessive thermodynamic penalty, is likely to provide optimal levels of catalytic activity.

Computational Details

A broad range of computational techniques have been used previously to investigate MgO surface chemistry, defects and dopants. Numerous studies have shown that a small, cation-terminated cluster of atoms embedded in a point charge array gives a reasonable representation of the electronic structure, which can be improved by the incorporation of long-range ploarization effects.[9,10]

We make use of an embedded cluster quantum mechanical/molecular mechanical (QM/MM) methodology[1] implemented in the ChemShell code.[11,12] A small number of atoms (i.e. those in close proximity to the defect and adsorbates) are treated using *ab initio* methods as implemented in the code GAMESS-UK[13] while simultaneously the GULP code performs calculations on a spherical or hemispherical array of several thousand additional atoms using interatomic potentials.[14–16] ChemShell and the structural optimization code DL-FIND[17] manage the interaction between the two systems, allowing the QM calculation to benefit from the presence of an electrostatic environment which can undergo long-range polarization in response to changes in the charge density around the site of interest. Further details of the QM/MM method are provided in our earlier work and in other literature[1,2,12,17,18]

In order to maintain consistency with our previous work and to allow for facile comparison with as much pre-existing literature as possible, we have used the B3LYP[19–21] exchange-correlation functional and the Def2[22] TZVP (for C, O and H), and QZVP (Mg) basis sets, with removal of the most diffuse functions (any P functions with tails extending beyond 5Å, as well as all F and G functions) which could have resulted in unphysical behaviour due to the spreading of charge density out of the QM region under the influence of the surrounding point charges. Placement of 10-electron effective core potentials on cation sites at the QM/MM boundary is also necessary to prevent unphysical polarisation of the charge density within the QM region. Interatomic potentials consisted of Lennard-Jones and Buckingham terms, with rigid ion Mg atoms and shells on O atoms, optimised for embedded cluster calculations. Counterpoise corrections were initially included for the adsorption energies of CO_2 at the defect site following a distance-based approximation outlined in our previous work, but are excluded within the catalytic cycle outlined below, as no correction was included to account for the addition of hydrogen due to its comparatively small basis set.

The full QM/MM cluster measured 60Å in diameter, centered on an oxygen vacancy. The outermost 5Å of the cluster had all atoms frozen in their bulk positions (as determined by prior relaxation using GULP), while all atoms within a radius of 25Å of the cluster origin were allowed to relax. This gives a total of 6433 atoms in the whole cluster, of which around 3700 were free to relax. The accuracy of the treatment of the outermost 7Å of relaxing MM atoms is reduced due to their interatomic potential cutoff values lying outside the range of frozen atoms present. However this still leaves an 18Å thick region surrounding the defect site to give an accurate reproduction of the effect of long range polarization.

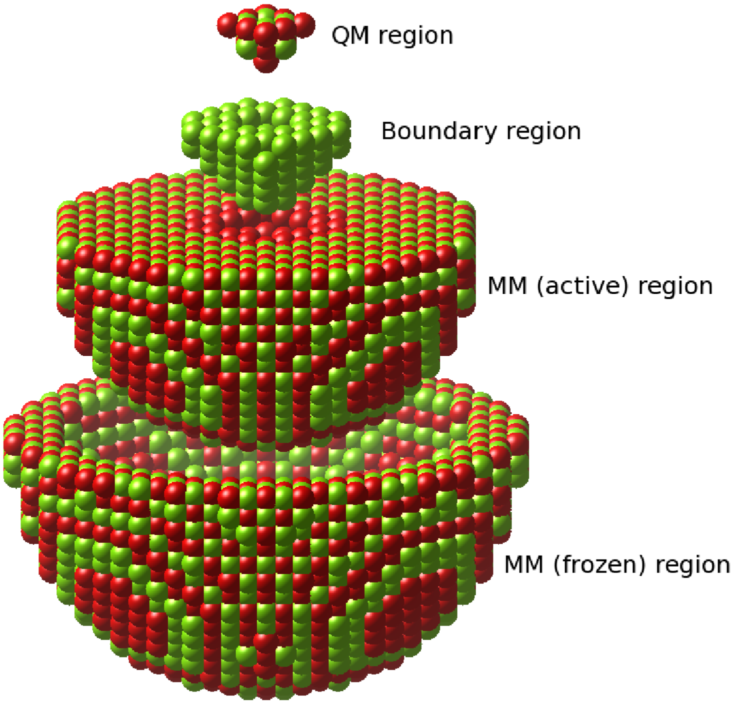

Figure 1: The embedded cluster setup used within ChemShell. Moving from top to bottom: the all-electron QM region (22-29 atoms, depending on the number of adsorbate atoms present); the cation-only large-core ECP region forming the QM/MM boundary; the relaxing MM ions; and the frozen MM ions. The outermost shell, containing point charges which are placed to ensure the Madelung potential in the centre of the cluster is accurately reproduced, has been omitted for clarity.

Results

In our previous work,[8] we determined that the most likely candidate for use in a catalytic reaction was the CO_2 chemisorbed at an F^+-centre, aligned normal to the surface, shown in Figure 2. CO_2 adopting this structure displayed exothermic binding to the defect site as well as a high degree of electron localization onto the adsorbate molecule. We note that a localized single electron at a surface oxygen vacancy site has been proposed as the active site for CO_2 conversion to methanol on ZnO.[23] Other possible sites such as CO_2 adsorbed at the F^0-centre were considered in the first hydrogen addition stage; however none gave rise to a more thermodynamically stable product and were therefore not considered further.

In our calculations, pairs of hydrogen atoms were seqentially introduced to the surface-adsorbate complex, corresponding to the addition of up to three H_2 molecules. In each case, H_2 was introduced to the surface-adsorbate complex calculation by adding a hydrogen molecule in the vicinity of likely adsorption sites (e.g. near the carbon atom of the surface bound CO_2), as well as in starting configurations which do not preserve the bonding of the hydrogen molecule (e.g. one H atom bound to the surface, the second to the adsorbate), before relaxation. Reaction processes requiring pre-adsorption and heterolytic dissociation of H_2 were not considered, as this process has a relatively high energy cost on the MgO (100) terrace of 77.71kJ/mol based on our calculations using a defect-free cluster (other sources place this value even higher at around 173.7kJ/mol).[24] Heterolytic dissociation may however play a role in reactivity at low-coordinated sites.[25,26] Dissociation at a neighbouring F^+-centre was also considered, having a lower energy cost of 25.07kJ/mol. However, adsorption and dissociation of H_2 at such a defect would have the disadvantage of deactivating the catalytic site, as one hydrogen atom fills the vacant oxygen position while the other forms a nearby OH group. Given their high formation energy and mutual electrostatic repulsion, the terrace is expected to be sparsely populated with F^+-centres and so migration of hydrogen atoms between them can be expected to play only a very limited role in the reaction processes described here.

The minimum energy structure obtained after hydrogen adsorption was carried forward to the next H_2 addition step, with other higher energy routes also considered if they were thought to lead towards a significantly more stable species. Due to the number of possible hydrogen atom positions and adsorbate orientations, there were several elementary steps between each of the identified minima and therefore activation barriers are not considered: our aim is to chart a range of intermediates in the CO_2 conversion reaction.

The proposed cycle is shown in Figure 3. The first step involved the adsorption of CO_2 at the F^+-centre to give structure B, with an exothermic adsorption energy of -132.3kJ/mol, which is followed by the addition of one hydrogen atom to the carbon of the adsorbed CO_2 to give a surface-bound formate ion with the second hydrogen forming an O-H bond with the surface, as shown in structure C. Other structures investigated included the addition of both H atoms to the adsorbate (on either the carbon or upper oxygen atom) as well as the shift of the surface-bonded hydrogen to other O_{5c} sites. Configurations with both hydrogen atoms bonded to the adsorbate were generally not stable, relaxing to the structure shown or to one with an alternative surface hydroxyl site (structures with one hydrogen bound to the CO_2 and the other to the surface are approximately equal in energy regardless of the positioning of the surface hydroxyl group). All structures investigated in this initial stage were stable with respect to molecular H_2, with the lowest energy configuration having a chemisorption energy for H_2 of around -115.1kJ/mol.

The addition of a second pair of hydrogen atoms led in the most favourable case to the dissociation of the CO_2 adsorbate to a molecule of H_2O and a formaldehyde molecule bound to the defect site via the oxygen atom, which sits close to the position necessary in order to re-form the defect-free (100) surface. This structure (labelled D) shown in Figure 3 was the most stable configuration identified, but formation was unfavourable with respect to dissociation of the second pair of hydrogen atoms to form H_2 by around 3.2kJ/mol. Localization of the unpaired electron onto the carbon atom was enhanced by the breaking of the upper C-O bond. The removal of water and formaldehyde from structure D could in principle lead to the regeneration of the F^+-centre to give a closed cycle, although this step is endothermic by 273.6kJ/mol.

On addition of a third pair of hydrogen atoms, the most energetically favoured process identified was the regeneration of a defect-free MgO surface with an OH-group coordinated to a surface magnesium ion and two protons forming hydroxyl groups with surface oxygen anions, plus the formation of the radical CH_3, shown in structure E. A reaction energy of -66.8kJ/mol (relative to the previous structure and a gas phase H_2 molecule) was calculated. The formation of methanol over a positively charged MgO surface with two adsorbed hydrogen atoms was also identified and found to be exothermic (structure F), although to a lesser extent than the first structure, at approximately -29.6kJ/mol. This result suggests that a reaction process to form methanol is possible, although the major product will be the CH_3 species and products of its subsequent reactions with other small molecules.

Formation of a surface-bound methoxy group (-O-CH_3) was not found to be favourable on the vacant site at any stage of the sequential H_2 adsorption process, which is probably a consequence of the positive charge and unpaired electron, which lead to the dissociation of a methoxy group to CH_3 and OH in the presence of hydrogen atoms adsorbed at the surface.

The addition of a fourth H_2 to the surface in the presence of the radical species enables the formation of a methane molecule and release of H_2O from the surface, leaving two hydrogen atoms adsorbed to MgO^+, the same structure seen after the formation and desorption of methanol. The final stage necessary to close the reaction cycle after formation of either methanol or methane is the regeneration of the F^+ site and removal of the two hydrogen atoms adsorbed to the surface. Previous work has however shown that for an F^0-centre water desorption would be an endothermic process[27] and is therefore likely to be a significant limiting step, an observation we confirm with the determination that desorption of H_2O to leave behind the required F^+-centre is endothermic by 170kJ/mol. Within both structures F and G, the unpaired electron density is distributed over the surface-layer magnesium atoms in the first nearest-neighbour shell around the filled vacancy.

The three catalytic cycles can be summarised as follows:
$CO_2 + 2H_2 \rightarrow CH_2O + H_2O$, $\Delta E = 29.47$kJ/mol (endothermic)
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$, $\Delta E = -76.77$kJ/mol (exothermic)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta E = -201.89$kJ/mol (exothermic)

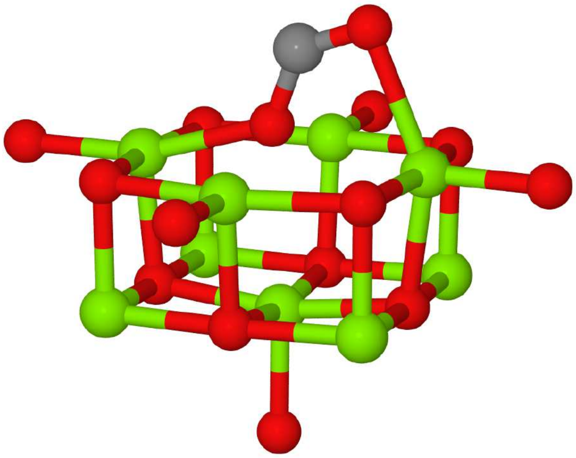

Figure 2: Geometry obtained after relaxation of CO_2 in proximity to an F^+ centre. O atoms shown in red, Mg in green and C in grey.

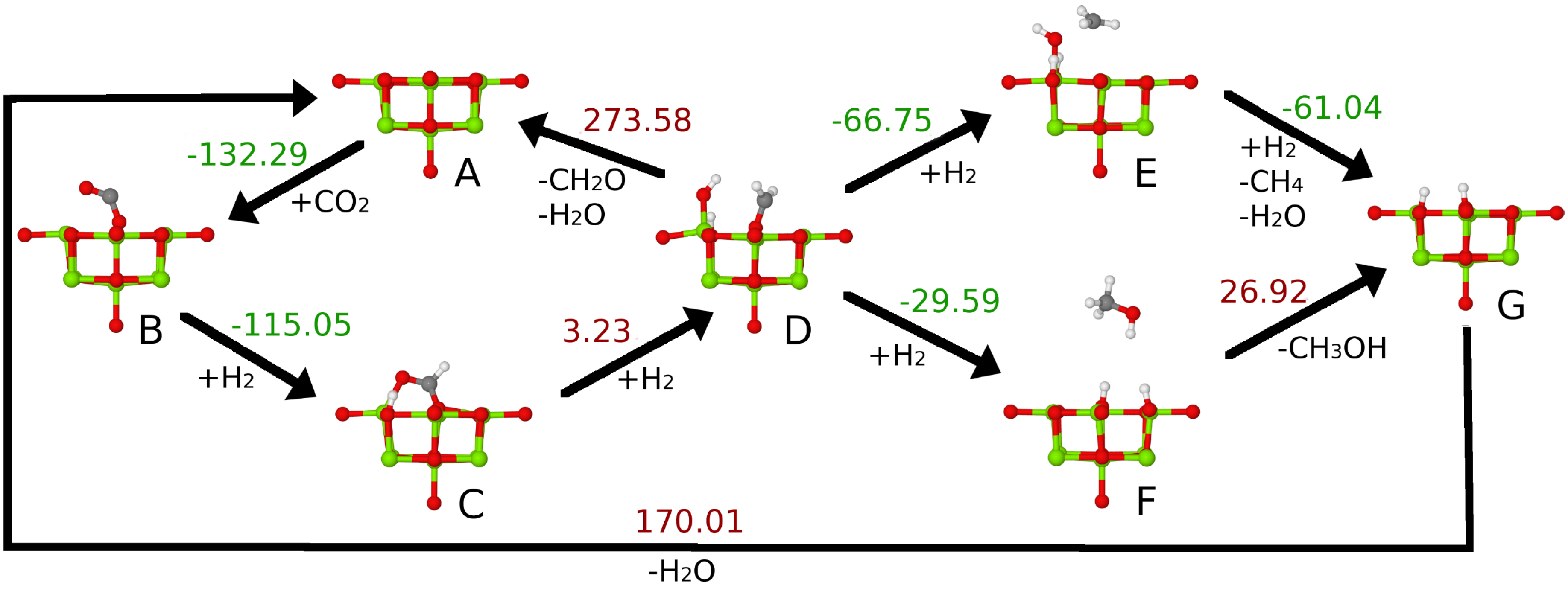

Figure 3: Catalytic cycles identified for the addition of CO_2 and H_2 to an F^+-centre. O atoms shown in red, Mg in green, H in white and C in grey. Energy changes for each step given in kJ/mol, with green and red representing exothermic and endothermic processes respectively. Key structures are as follows: A - Unmodified F^+-centre, B - CO_2 adsorbed at F^+-centre, C - 2×H adsorbed on structure B (one on the MgO surface, one on the CO_2 adsorbate), D - H + OH adsorbed on MgO surface, CH_2O bound to F^+-centre, E - 2×H + OH adsorbed on MgO surface, CH_3 radical formed, F - 2×H adsorbed on MgO^+ surface, CH_3OH formed, G - 2×H adsorbed on MgO^+ surface. Unpaired electron density for structures A, F and G is distributed over the surface-layer magnesium atoms in the first nearest-neighbour shell around the filled vacancy. For all other structures, the spin density is predominantly localised on the carbon atom of the adsorbate/product.

Discussion and Conclusions

As in the case of methanol synthesis over ZnO, the greatest challenge appears to arise due to the tendency for oxygen atoms to remain bound to defect sites after the initial reaction processes are complete. In the ZnO case, this effect causes the cycle to be shifted from the catalytic conversion of CO_2 to the consumption of CO, although a cycle such as those described here where an additional molecule of H_2 is used to regenerate the active site is also feasible.

For MgO, the route is altered by the need for ionization to give the desired single-electron oxygen vacancy. This shortcoming can be in principle be avoided through the use of alkali-metal doping, such as in the well-studied case of Li-MgO;[28] however the presence of paramagnetic centres due to Li-doping is disputed.[29] An additional factor which may contribute to the viability of single-electron oxygen vacancies as active sites is the use of ultrathin MgO films, which have been shown to allow for F^+-centres to be favoured over the generally more stable F^0 oxygen vacancy with two localized electrons.[30]

It has been noted[31] that the populations of F^0 and F^+ defects, particularly on the (100) terrace, are expected to be very low and therefore of limited relevance to an operating catalytic system. The alternative single-electron site proposed by Pacchioni, the $(H^+)(e^-)$ species, should be considered in relation to CO_2 reactivity in the future.

Overall, while MgO may not itself play a major role in efforts towards CO_2 recycling processes, the general principle of using oxygen vacancies as an active site will be applicable to other metal oxide catalysts.

In particular, future work should focus on transition metal oxides where the balance between Madelung potential driven electron localisation and redox behaviour at the metal site will determine both how prevalent surface oxygen vacancies are, and the availability of electrons necessary for the formation of an activated CO_2 species.

Acknowledgements

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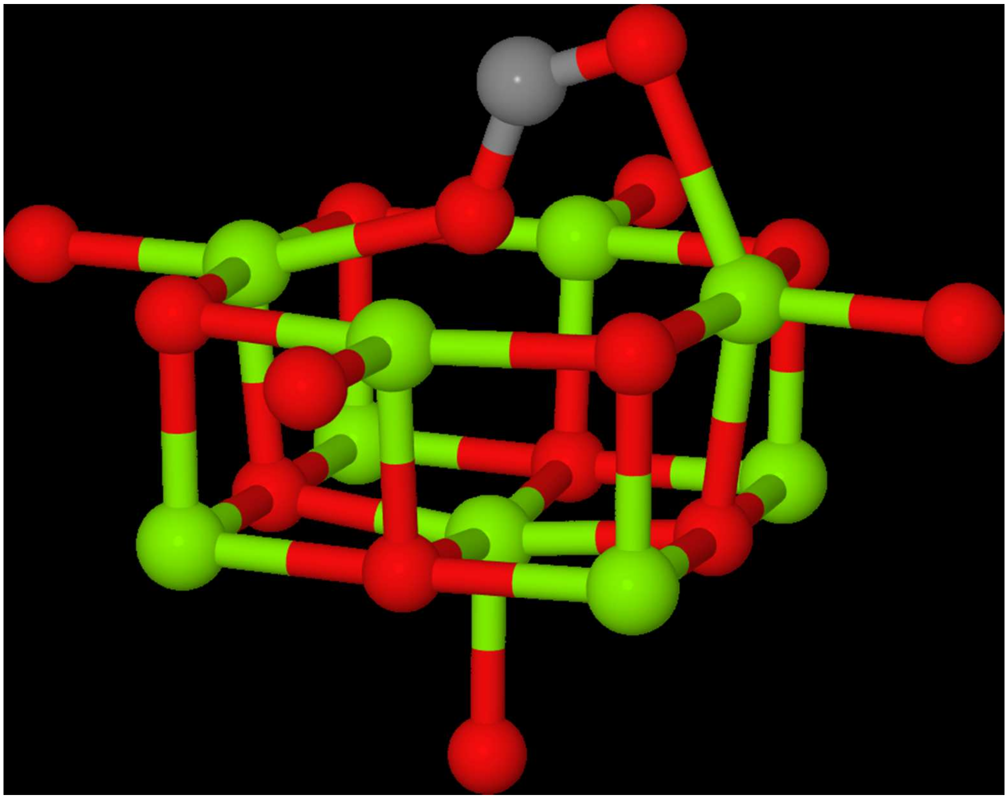

A series of model catalytic cycles for CO_2 conversion at metal oxide surface vacancy sites is presented.