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THEORETICAL STUDIES OF THE STRUCTURE AND PROPERTIES OF COBALT-SUBSTITUTED ALUMINOPHOSPHATES

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Abstract

There has been considerable debate regarding the structure and properties of cobalt-substituted aluminophosphate catalysts. In particular, the coordination environment, Co-O bond lengths and oxidation state are all thought to have important effects on the catalytic effectiveness of the material. This paper uses both atomistic modelling and quantum mechanical based methods to probe the local structure both of possible framework and extra-framework cobalt sites. We find that in the case of tetrahedral geometries, the bond lengths are similar to those found in cobalt oxides and measured from EXAFS experiments. The attractiveness of the cobalt sites for the direct binding of molecular oxygen is also investigated to assess the likelihood of the use of this oxidant in a catalytic process. In order to benchmark our computational methods calculations are also performed on a model biological system which is known to bind molecular oxygen reversibly. We find no evidence for direct oxygen binding in the zeolite models for a five coordinated framework cobalt centre.

1. Introduction

Titanium-substituted zeolites, such as TS-1, are used to catalyse many oxidation reactions using hydrogen peroxide as the oxidant. Since there are environmental concerns related to the use of hydrogen peroxide, the use of molecular oxygen as an alternative oxidant would be desirable. However, it is known that only the late transition metals (such as Co, Mn and Cr) perform oxidations directly with O$_2$.\textsuperscript{1} It is possible to hypothesise a system in which the first metal binds O$_2$, activates it and then transfers it to the titanium centre to affect the catalysis. As the first part of a theoretical investigation of the plausibility of such a system, this paper investigates the possibility of molecular oxygen binding directly to a transition metal centre in a zeolite.

It is important to benchmark our computational methods on a system that is known to bind molecular oxygen experimentally. We decided initially to perform calculations on the Co chelate system, N,N'-ethylenebis(salicylidiminato)cobalt(II) on which extensive structural and thermochemical data has been measured.

Since, in general, it is more likely that an extra-framework cation site has a more open coordination geometry than a framework site, both types of cobalt substitution were considered. For the framework sites, we constructed quantum mechanical clusters based on the AFI framework with cobalt substitution and investigated them for oxygen
binding. For the extra-framework sites, there is no structural data on cation location, so Monte Carlo docking calculations were performed to assess likely binding sites. Using this data, clusters were constructed and oxygen binding investigated as before.

2. Computational Details

This work features a number of different computational approaches. The docking and energy minimisation calculations using a molecular mechanics approach based on the ionic model. They were carried out using the DIZZY software. The quantum mechanical calculations were performed using the GAUSSIAN94 software. All calculations were executed on a four-processor SGI Origin200 workstation.

3. Results and Discussion

Quantum chemical calculations were performed on the model cobalt chelate complex, N,N'-ethylenbis(salicyldeniminato)cobalt(II) (Figure 1) which experimental studies have shown to bind molecular oxygen in the presence of pyridine to form a six-coordinate complex, Co(salen)(pyr)(O2).

The calculations were performed using density functional theory with the B3LYP hybrid functional. We found that it was necessary to employ an all-electron basis set (6-311G) on cobalt rather than the available pseudopotentials (LANL1DZ and LANL2DZ) in order to give a significant binding energy (Table 1).

![Figure 1: Co model complex for molecular oxygen binding](image)

Table 1: Calculations on Co(salen) complex

<table>
<thead>
<tr>
<th>Co basis</th>
<th>E_{bind} (kcal mol^{-1})</th>
<th>r(Co–O) (Å)</th>
<th>r(O–O) (Å)</th>
<th>θ(Co–O–O) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-311G</td>
<td>-16.5</td>
<td>1.90</td>
<td>1.29</td>
<td>115.6</td>
</tr>
<tr>
<td>LANL1DZ</td>
<td>+0.2</td>
<td>2.90</td>
<td>1.21</td>
<td>119.6</td>
</tr>
<tr>
<td>LANL2DZ</td>
<td>-0.2</td>
<td>2.38</td>
<td>1.23</td>
<td>119.6</td>
</tr>
<tr>
<td>experiment^5</td>
<td>-12.4</td>
<td>1.95(5)</td>
<td>1.34(3)</td>
<td>116</td>
</tr>
</tbody>
</table>

We are unaware of any crystallographic studies on framework substituted cobalt in the AFI structure so the precise coordination and Co–O bond lengths are uncertain. However, there have been extensive EXAFS measurements made on this system which suggest Co–O distances of about 1.92Å, and also some evidence for an asymmetric coordination environment involving one long and three short Co–O bond lengths.
Initially we constructed small cluster models with only two T-sites (cobalt and phosphorus) for quantum mechanical calculations. However, termination of these clusters proved troublesome. Termination with hydroxyl groups led to unrealistic hydrogen bonds to form during geometry optimisation which distorts the local geometry, whereas termination of the cobalt with hydrogen causes the formation of a hydrogen molecule on optimisation.

To alleviate these difficulties, we considered a cluster in which cobalt is fully tetrahedrally coordinated to adjacent phosphorus tetrahedra terminated with hydrogens (Figure 2). In the case of the Co(II) cluster which is a d⁷ system, a perfectly tetrahedral geometry would produce a quartet ground state. However, any small distortions from this would remove the degeneracy of the t₂ levels and give the possibility of a doublet. Both spin states were considered. Two geometries were produced after full geometry optimisation. The results are shown in Table 2. The quartet gave the lowest energy eigenstate and an average Co–O bond length of 1.95Å. This can be compared with Co(II) in an octahedral site (2.13Å in CoO) and Co(II) in a tetrahedral site (1.93Å in Co₂O₃). The Co(III) system has singlet and triplet possible spin states since it is a d⁶ system. In this case, the triplet is found to be the ground state with a bond length of 1.84Å. There is only one example of Co(III) in a tetrahedral geometry in the heteropolytungstate, K₅CoⅢO₅W₁₂O₃₆·20H₂O, where the bond length is 1.88Å.

<table>
<thead>
<tr>
<th>cluster</th>
<th>ground state</th>
<th>average Co–O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)(OPH₃)₄</td>
<td>doublet</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>quartet†</td>
<td>1.95</td>
</tr>
<tr>
<td>Co(III)(OPH₃)₄</td>
<td>singlet†</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>triplet†</td>
<td>1.84</td>
</tr>
</tbody>
</table>

† indicates lowest energy eigenstate

In order to assess the possibility of the binding of molecular oxygen to framework cobalt, we took the optimised geometries from the previous section and introduced molecular oxygen as a fifth ligand. In the Schiff’s base complexes, the binding is accompanied by a partial charge transfer from the cobalt dₓ₂-orbitals to the π* orbitals.
in oxygen and a spin pairing, so we assume here that the spin states of the zeolite-oxygen complexes remain the same as in the last section. In each case, the oxygen is repelled by the zeolite fragment and no binding is observed.

In order to determine possible extra-framework binding locations for Co(II) in AFI, a Monte Carlo docking calculation was performed. Twenty trial insertions were performed and each minimised to produce a set of binding positions. Since we are only interested in sites that could cause catalysis, the insertions are restricted to the 12-ring channel. Initially, the pure AlPO structure was considered. Only one binding site was observed that was sufficiently accessible to allow molecular oxygen to approach. This binding site is located approximately centrally on the six-ring in the wall of the 12-ring channel. The closest contacts observed are at 2.2Å and the coordination of the Co(II) cation is approximately square pyramidal. This geometry is similar to that observed in transition-metal substituted aluminosilicates.

Using the binding site predicted in the previous section, several quantum mechanical clusters were constructed of varying sizes and terminated with hydroxyl groups. The largest cluster consisted of the six-ring structural element and all nearest neighbour T-sites with the stoichiometry, CoP₉Al₉O₂₁(OH)₃₀. Due to the size of this model, the STO-3G basis was used for P, Al, O and H, while retaining 6-311G for cobalt and 6-31G* for O₂. The outer hydroxyl groups were held fixed during optimisation. As with the framework models, no oxygen binding was observed.

4. Conclusion

Within the scope of the five-coordinated cluster models studied here we find no evidence to suggest that molecular oxygen can bind directly to a framework cobalt-substituted AlPO. We are now working on models with higher coordination numbers to assess the effect of other ligands on the possible enhancement of the binding process.

References