

# On the formation of titanyl (Ti=O) groups in mesoporous and microporous titanasilicate catalysts: a computational study

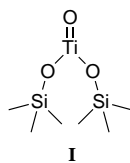
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Density functional theory calculations are reported which suggests that titanyl groups,  $\text{Ti}^{\text{IV}}=\text{O}$ , can form by relatively low energy pathways in titanium(IV) silicate catalysts, thereby providing a possible route to the active oxygen donating site responsible for partial oxidation reactions in these materials.

Knowledge of the structure and chemical properties of the active site in any catalytic reaction is critical to the understanding of the detailed reaction mechanisms. Industrially important examples are provided by the partial oxidation processes over titanium(IV) framework silicates<sup>1</sup> exemplified by TS-1, TS-2<sup>2</sup> and Ti-MCM-41.<sup>3–5</sup> These reactions occur essentially in the liquid phase involving reactant, solvent, sacrificial oxidant such as  $\text{H}_2\text{O}_2$  or  $\text{Bu}^t\text{OOH}$ , and the titanium(IV) substituted heterogeneous catalyst. Use of  $\text{Ti}^{\text{IV}}$  embedded in some manner into a silicate framework produces a catalyst with the desirable qualities of guest molecule shape selectivity and one in which oxidation is effected with very high turnover rates and selectivities with respect to both the reactant and the sacrificial oxidant.<sup>5–9</sup> Although it is becoming increasingly evident<sup>5,8</sup> that  $\text{Ti}^{\text{IV}}\text{OH}$  centres tripodally attached by O to Si are the major sites for catalytic activity in these systems, a number of questions concerning intermediate titanates still remain. This work reports first principles quantum chemical calculations in order to derive possible models for titanium containing species that could occur on the reaction coordinate to formation of the active oxygen donating species in these systems.

One of the earliest suggestions for the nature of these titanium containing species (originally with respect to  $\text{Ti}^{\text{IV}}$  incorporated into amorphous silicates) was that of a titanyl group stabilised by the silicate host (species **I**, Fig. 1).<sup>10,11</sup> It has been suggested that this titanyl species is responsible for the very high oxidation capacity of titanium(IV) silicates. Titanyl groups have not, however, been observed in TS-1 or similar catalysts unlike its unambiguous characterisation (albeit in a state of five coordination) in the mineral fresnoite<sup>12</sup> and the synthetic layered titanasilicate JDFL-1.<sup>13</sup> Indeed, the lack of UV–VIS absorption corresponding to species **I**<sup>14</sup> has been taken by many to indicate that this species is not present in these materials. Species **I** can, however, account for a number of experimental observations such as the catalyst's IR and NMR responses and its behaviour in  $^{18}\text{O}$  labelling experiments.<sup>15</sup> Many workers, however, favour the model of  $\text{Ti}^{\text{IV}}$  in four-coordinate sites within the framework, (Fig. 2, species **II**), or grafted onto the surface of a silicate material, (Fig. 2, species **III** and **IV**).<sup>5,7,16,17</sup> Species **III** and species **IV** illustrate the hydroxide forms of the  $\text{Ti}^{\text{IV}}$  sites.

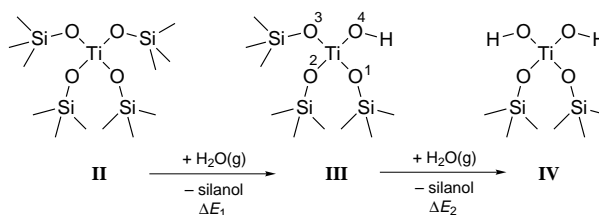


**Fig. 1** Schematic representation of a titanyl ( $\text{Ti}=\text{O}$ ) group, a species suggested as a possible titanium(IV) oxygenate in titanium(IV) silicate catalysts

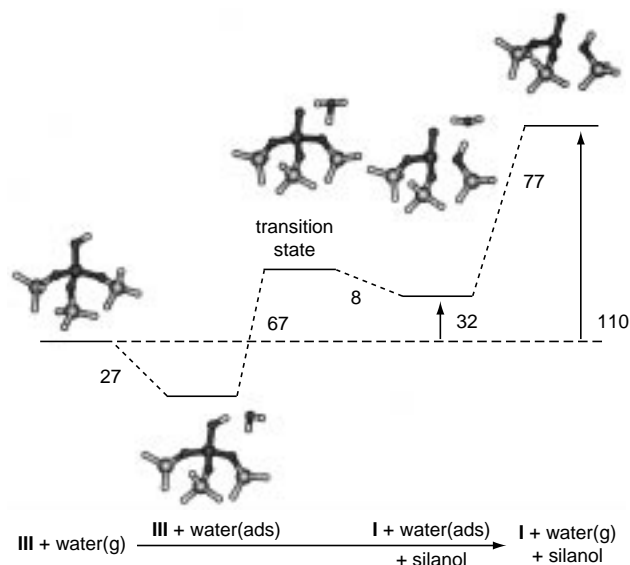
Organic derivatives have also been prepared<sup>18</sup> and it is noted that these catalysts may behave differently. It is also noted that Fig. 2 represents the state of the  $\text{Ti}^{\text{IV}}$  centres in a dehydrated system. Expansion of the  $\text{Ti}^{\text{IV}}$  coordination shell on addition of coordinating solvents such as water has now been well characterised both experimentally<sup>1,16</sup> and computationally.<sup>19</sup> The partial hydrolysis of the  $\text{Ti}-\text{OSi}$  bonds in the absence of coordinated water can also be described in terms of species **II**, **III** and **IV** (see the reaction at the bottom of Fig. 2).<sup>17</sup>

Recently, we have reported first principles, density functional theory cluster calculations of the processes shown in Fig. 2,<sup>19</sup> *i.e.* over the hydroxide forms of the catalyst. Using a  $\text{H}_3\text{SiOH}$  fragment to model the silanol species produced during the hydrolysis and calculating the energy differences at infinite separation of the silanol and the hydrolysed  $\text{Ti}^{\text{IV}}$  fragment, the internal energies,  $\Delta E_1$  and  $\Delta E_2$ , were calculated to be 20 and 22  $\text{kJ mol}^{-1}$ , respectively. However, given that in an actual silicate system the hydrolysed titanium(IV) hydroxide complex and the resulting silanols would be in hydrogen-bonding distance, and that typical hydrogen-bond energies are of the order of 20  $\text{kJ mol}^{-1}$ , it is expected that a mixture of species **II**, **III** and **IV** would be present in systems where  $\text{Ti}^{\text{IV}}$  is isomorphously substituted into the silicate framework, *e.g.* TS-1;<sup>17</sup> and a mixture of species **III** and **IV** would be present in systems where  $\text{Ti}^{\text{IV}}$  is grafted onto a silicate surface, *e.g.* the titanium(IV) hydroxide form of surface grafted Ti-MCM-41.<sup>5</sup> We also showed that within the cluster approximation and in the absence of any adsorbates the formation of species **I** from **III** was energetically unfavourable (requiring 110  $\text{kJ mol}^{-1}$ ). We now report on new computational evidence suggesting that species **I** is energetically accessible from the hydroxide form of titanium(IV) silicates, species **III** and **IV**, in the presence of water and/or other protic solvents.

Fig. 3 shows the calculated reaction profile for formation of species **I** from **III**, unsolvated and in the presence of one molecule of water. The geometries and energies were optimised using the Becke–Perdew'86 gradient corrected density functional included self-consistently in all stages of the calculation as implemented in the Cray Research code DGauss 3.0<sup>20</sup> (a 'fine' integration grid was also employed). A valence double-zeta basis set with polarisation functions on non-hydrogen atoms (DZVP) was used throughout. This method has now been used for a number of problems in the field of silicate chemistry and is known to give reliable geometries and binding ener-



**Fig. 2** Schematic representation of possible four-coordinate titanium(IV) oxygenates in titanium(IV) silicate catalysts. The process shown at the bottom of the figure illustrates the hydrolysis of these species in the presence of a single molecule of water.



**Fig. 3** DFT optimised reaction path for the formation of a titanyl group (species **I**), modelled by  $(\text{H}_3\text{SiO})_2\text{Ti}=\text{O}\cdot\text{HOSiH}_3$ , from a silicate embedded titanium hydroxide (species **III**), modelled by  $(\text{H}_3\text{SiO})_3\text{TiOH}$ , in the presence of a single molecule of water. Energies are in  $\text{kJ mol}^{-1}$ .

gies.<sup>21,19,22</sup> Activation barriers are more problematic and are generally accepted to be underestimates.<sup>23</sup> The cluster model for the hydroxide species **III**,  $(\text{H}_3\text{SiO})_3\text{TiOH}$ , was fully optimised with respect to all atomic degrees of freedom. All other clusters models were then optimised under the constraint that the Si coordinates were fixed at the values obtained from the cluster model of species **III**. These constraints were enforced to prevent unrealistic relaxation of the cluster. This does however introduce an unknown error into the calculated energy changes for the hydrolysis reaction due to structural strain. The strain is difficult to estimate without resorting to computationally prohibitive clusters, for example, 'closed' cubic silasesquioxanes. The error will however be system- and site-dependent although it is likely that the constraints imposed in the current calculations will lead to the energy changes being unable to relax (under the constraints imposed by the silicate host).

Clearly the process shown in Fig. 3 is essentially one of proton transfer from  $\text{O}^4$  to one on the other oxygens  $\text{O}^1$  to  $\text{O}^3$  (Fig. 2) and is thus dependent on one of the hydroxide forms of  $\text{Ti}^{\text{IV}}$  being present. It is also clear that, as described above, unsolvated species **III** is much more stable than species **I**. In the presence of a single molecule of water however, titanyl species **I** can be formed with a true activation barrier of  $67 \text{ kJ mol}^{-1}$  or an effective barrier of  $40 \text{ kJ mol}^{-1}$  with respect to the original reactants. Furthermore, in the presence of a single water molecule, species **I** is only  $32 \text{ kJ mol}^{-1}$  less stable than the separated titanium(IV) hydroxide (species **III**) and water, a change of  $77 \text{ kJ mol}^{-1}$  with respect to the unsolvated case. Despite the hydrophobic nature of TS-1 and similar silicates, small amounts of water and/or other protic solvents (generated, for example, during oxidation reactions) will be present enhancing the probability of forming titanyl species **I** from any accessible titanium(IV) hydroxide groups.

At present, no account of the environment of the  $\text{Ti}^{\text{IV}}$  site has been included within the calculations. However, if we examine the calculated change in the dipole moment ( $\mu$ ) of the complexes leading to the transition state for formation of titanyl species **I**, we note that activation results in an increase in  $\mu$  [ $3.23\text{--}4.21 \text{ D}$  ( $1 \text{ D} \approx 3.336 \times 10^{-30} \text{ C m}$ )]. We expect therefore that the environment provided by a partial ionic silicate framework would stabilise the transition state more than the solvated titanium(IV) hydroxide (species **III**) and that the

calculated activation barrier shown in Fig. 3 would therefore be an overestimate. It is also expected that the real barrier would be strongly correlated with the topological position of the titanium(IV) complex within the host framework as well as with the chemical composition of that framework.

In conclusion, we have employed density functional theory methods to show that titanyl groups, *i.e.* species **I**, can be formed with relative ease from the hydroxide forms of four-coordinate titanium(IV) silicates in the presence of even small amounts (in this case one molecule) of water and probably other protic solvents. Their formation is likely to be correlated with the precise nature of the  $\text{Ti}^{\text{IV}}$  environment. However, given that the limiting case of aqueous  $\text{TiO}_2^{2+}$  is known to be a very labile species (oxygen exchange rate estimated at  $16\,000 \pm 5\,000 \text{ s}^{-1}$  at  $298 \text{ K}$ )<sup>24</sup> and that no  $\text{Ti}=\text{O}$  UV-VIS absorption has been measured in silicates, titanyl species are probably very short-lived species in dynamic equilibrium with the hydroxide species **III** and/or species **IV**. We suggest however, on the basis of the current calculations, that they could be present in sufficient concentration to provide a route to the active oxygen-donating species for partial oxidation catalysis in hydroxide forms of titanium(IV) silicates.

The authors would like to thank Professor Sir J. M. Thomas, Dr Sankar and Dr Oldroyd both of the Royal Institution of Great Britain for useful discussions and collaboration. P. E. S. would also like to thank EPSRC for financial support and computer resources.

## Footnote and References

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Received in Cambridge, UK, 30th June 1997; 7/04567K