Simulation Study of Copper(I) and Copper(II) Species in ZSM-5 Zeolite

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Low energy configurations of Cu^I and Cu^{II} species in the ZSM-5 zeolite, probed by energy minimisation techniques, are found to be bound strongly to framework aluminium or copper species.

Copper, when appropriately introduced into the ZSM-5 zeolite, has been shown to catalyse the decomposition of NO into N_2 and O_2. However, the catalyst decomposes at high temperatures[1] and there is therefore a major incentive for the development of similar catalysts which are thermally stable. In guiding the design of such a catalyst it would be most valuable to have detailed knowledge of the active sites. At present there is considerable debate about the nature of both the reaction mechanism and the active site.[1–9] In particular, it is uncertain whether the site comprises coordinatively unsaturated single or paired Cu^I or Cu^{II} ions and where these are located within the zeolite channels. In this study we used computer modelling techniques to examine the stability of various possible models for active sites in this catalyst.

The preparation of Cu-ZSM-5 can be achieved by mixing copper acetate with Na-ZSM-5. It is expected that the copper species exchange with Na^+ and occupy extra-framework sites within the channels of the ZSM-5 zeolite. We therefore examined the energetics of Cu^+ and Cu^{2+} species at extra-framework positions firstly within the purely siliceous zeolite silicalite, and next in ZSM-5.

The idealised structure of silicalite[10] comprises interconnecting straight (5.7 × 5.2 Å) and sinusoidal channels (5.6 × 5.3 Å). The synthetic zeolite ZSM-5 has the same framework structure as silicalite with a proportion of the silicon sites occupied by Al^{3+} species (Si : Al 4–95). The low temperature ZSM-5 zeolite has been determined by X-ray diffraction to be monoclinic (as opposed to the high temperature orthorhombic structure) with 24 independent T sites.[11] This subtle orthorhombic–monoclinic distortion has been successfully modelled using simulation techniques.[12] These and other calculations encourage confidence in the reliability of these methods.

The techniques used in this study have been described extensively elsewhere,[13] therefore only a brief overview is given here. We used what has become a very standard approach for calculating the energy of localised species in solids. Ions within a region close to the localised species (in this case the copper ions and relevant framework species, *i.e.* T-site Al^{3+}) were allowed to relax to zero force using a Newton–Raphson iterative minimisation procedure. In the present work this inner region contained 350 ions. The polarisation of the defect in the surrounding crystal lattice was calculated following the Mott–Littleton procedure.[14] This methodology has been implemented into the CASCADE code.[15] The interactions between ions within region I were described by long-range Coulombic interactions and short-range parameterised repulsive interactions. The directional properties of the covalent bonding were modelled using bond harmonic three body terms around the tetrahedral angle of the silicon atoms in the lattice. The electronic polarisability was introduced *via* the shell model.[16]

Table 1 Ionic charges and shell model parameters

Species	Charges	Spring constant/eV Å^{-2}
Si^{4+} core	4.0	rigid ion
O^{2-} shell	−2.869	74.92
O^{2-} core	0.869	
Cu^{2+} core	2.0	rigid ion
Cu^+ core	1.0	rigid ion
Al^{3+} core	3.0	rigid ion

Table 2 Short-range potential parameters of the form $E(r) = A\exp(-r/\rho) - Cr^{-6}$. Short-range cut-off = 20.0 Å

Species	A/eV	ρ/Å^{-1}	C/eV Å^{-6}
$Si^{4+}–O^{2-}$	1283.9	0.32052	10.66
$O^{2-}–O^{2-}$	22764.0	0.14900	27.88
$Al^{3+}–O^{2-}$	1460.3	0.29912	0.0
$Cu^{2+}–O^{2-}$	712.8	0.32698	0.0
$Cu^+–O^{2-}$	681.8	0.32582	0.0

The quality of the interatomic potentials exerts a crucial influence on the reliability of the results of the simulation study. In the present case, the parameters for the zeolite lattice were taken from the study of Jackson and Catlow,[17] whose reliability in modelling the structure of silicalite has been demonstrated previously.[12] The parameters for the Cu–O interactions were taken from Baetzold[18] who has shown them to model accurately the Cu–O bond distances in the orthorhombic $YBa_2Cu_3O_7$ crystal to within 0.02 Å. The potential parameters are reported in Tables 1–3.

We first identified the low energy sites for extra-framework copper species (Cu^+ and Cu^{2+}) in the purely siliceous zeolite, silicalite, before considering possible structures in ZSM-5. Cu^+ and Cu^{2+} ions were therefore placed at various extra-framework locations within the silicalite structure and the system allowed to relax. The lowest energy positions located for the extra-framework Cu^{2+} and Cu^+ are near the T12 and T7 sites, respectively. The Cu^{2+} ion is, as expected, located slightly nearer the zeolite wall compared with the Cu^+ ion. The nearest neighbour Cu–O(framework) distances are calculated to be 2.02–2.14 Å (4-coordinated) for Cu^{2+} and 2.66–3.02 Å for Cu^+ (3-coordinated). We note that the experimental Cu^{2+}–O bond lengths in Cu-ZSM-5 from EXAFS data[3] give a value of 1.96 Å.

Next, we considered ZSM-5 which contains a low fraction of aluminium at silicon framework sites. It is therefore pertinent to establish whether there is any association of extra-framework copper species with the framework Al^{3+}. As the low energy

Table 3 Three body terms of the form $E(\theta) = \frac{1}{2}K(\theta_o - \theta)^2$

Species	K/eV rad^{-2}	θ_o/°
$O^{2-}–Si^{4+}–O^{2-}$	2.097	109.47
$O^{2-}–Al^{3+}–O^{2-}$	2.097	109.47

Table 4 Association between Al^{3+} substituting for Si^{4+} and an extra-framework Cu^+ or Cu^{2+} ion

Cluster site	Cluster energy/eV	Binding energy/eV
Cu^+ (extra-framework) (T7)	−3.995	
Cu^{2+} (extra-framework) (T12)	−14.290	
Al^{3+} (T14)	38.425	
Al^{3+} (T14) + Cu^+	34.430	
Al^{3+} (T14) + Cu^{2+}	24.135	
[Al^{3+} (T7), Cu^+]	33.095	1.3
[Al^{3+} (T12), Cu^{2+}]	21.521	2.6

configurations of the extra-framework copper species identified are in close proximity to the silicon T12 and T7 sites for Cu^{2+} and Cu^{+}, respectively, we considered both Cu^{2+} and Cu^{+} close to an Al^{3+} substituted at framework T12 and T7 sites. We calculated binding energies for the species which we defined as the energy difference between the aluminium–copper pair and the component species, namely, copper at the lowest extra-framework position (near the framework T12 or T7 sites) and aluminium substituting for silicon at the T14 site. Al^{3+}(T14) is calculated to be energetically favourable with respect to the other T sites.[19] The binding energies obtained for the Cu–Al pair are 129 kJ mol^{-1} for Cu^{+} and 252 kJ mol^{-1} for Cu^{2+} (details are given in Table 4). Such high binding energies suggest that extra-framework copper species will be associated with framework Al^{3+} in accordance with recent photoluminescence studies.[7] The calculated nearest-neighbour Cu–O bond distances are 1.88–2.65 Å for a 5-coordinate system for the bound Cu^{2+} ion, compared with 2.02–2.14 Å for Cu^{2+} in silicalite. The 4-coordinated configuration of the latter distorted as the Cu^{2+} ion is displaced 0.35 Å closer to the Al^{3+}-substituted T12 site. The nearest-neighbour Cu^{+}–O bond distances are 2.43 and 2.45 Å (2-coordinated) for the bound Cu^{+} ion, compared with 2.66–3.02 Å for Cu^{+} in silicalite. The results show that the nearest-neighbour Cu–O bond distances and coordination number are significantly reduced as a result of the association between T-site Al^{3+} (which has an effective negative charge) and the extra-framework copper species.

We then addressed the question of whether it is possible to have stable species involving T-site Cu. To this end we first substituted Cu^{2+} for silicon at each of the 24 T sites of silicalite. The calculations suggested that Cu^{2+} substitution at the T2 site is energetically favourable with respect to the other T sites (Table 5). Next, Cu^{2+} was substituted for a framework silicon ion and an additional Cu^{2+} placed in close proximity in silicalite. The energies for various [Cu^{2+}(T*n*), Cu^{2+}] clusters are given in Table 6, where Cu^{2+}(T*n*) represents Cu^{2+} replacing Si^{4+} at the T*n* lattice site with an extra-framework Cu^{2+} in close proximity to the substituted copper ion. The binding energy is given relative to the component copper species: [Cu^{2+}(T2)] and [Cu^{2+}] at the lowest energy extra-framework position (near the T12 framework site). The lowest energy configuration located for the bound copper pair is with copper substituting at the T5 position. The nearest-neighbour Cu–O bond distances are now 1.83–1.91 Å for a 3-coordinate species for the bound extra-framework Cu^{2+} which compares with 2.02–2.14 Å for Cu^{2+} in silicalite. Fig. 1 shows the configuration of the [Cu^{2+}(T5), Cu^{2+}]

Table 5 Cu^{2+} substitution energies for the 24 T sites in silicalite

T Site	Substitution energy/eV	Energy relative to Cu^{2+}(T2)/ kJ mol^{-1}	T site	Substitution energy/eV	Energy relative to Cu^{2+}(T2)/ kJ mol^{-1}
T2	67.997	0	T9	68.157	15
T8	68.020	2	T12	68.168	17
T5	68.062	6	T10	68.190	19
T7	68.099	10	T22	68.198	19
T4	68.100	10	T23	68.204	20
T11	68.106	11	T21	68.229	22
T19	68.106	11	T20	68.237	23
T13	68.128	13	T15	68.266	26
T16	68.140	14	T17	68.273	27
T24	68.147	14	T14	68.292	28
T3	68.148	15	T1	68.334	33
T6	68.149	15	T18	68.391	38

Table 6 Association between Cu^{2+} substituting for Si^{4+} and an extra-framework Cu^{2+} ion

Cluster site	Cluster energy/ eV	Binding energy/ eV	Binding energy relative to [Cu^{2+}(T3), Cu^{2+}]/kJ mol^{-1}
Cu^{2+} (extra-framework)	−14.290		
Cu^{2+}(T2)	67.997		
Cu^{2+}(T2) + Cu^{2+}	53.707		
[Cu^{2+}(T5), Cu^{2+}]	47.014	6.69	0
[Cu^{2+}(T2), Cu^{2+}]	47.015	6.69	0
[Cu^{2+}(T4), Cu^{2+}]	47.026	6.68	1
[Cu^{2+}(T19), Cu^{2+}]	47.049	6.66	3
[Cu^{2+}(T11), Cu^{2+}]	47.188	6.52	17
[Cu^{2+}(T8), Cu^{2+}]	47.206	6.50	19

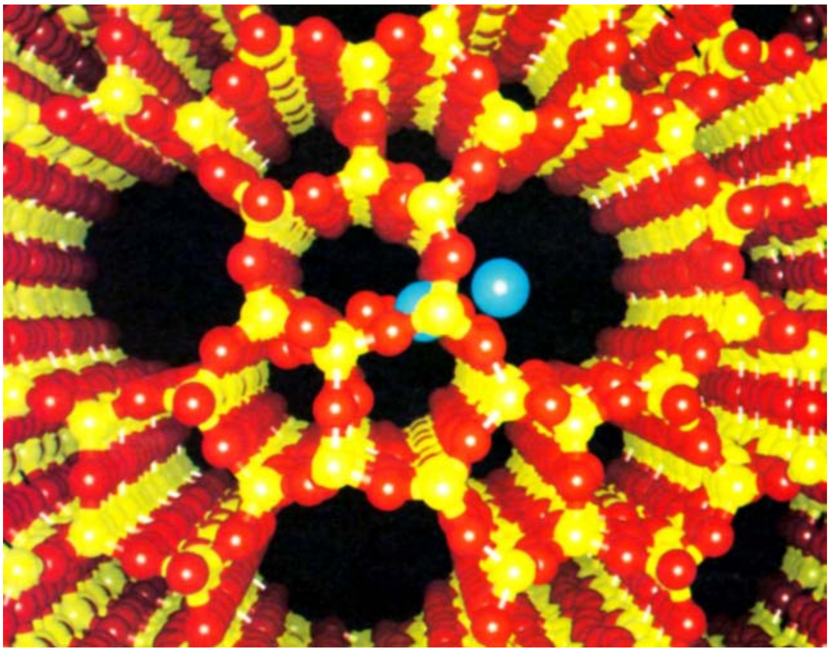

Fig. 1 Low energy configuration for the [Cu^{2+}(T5), Cu^{2+}] cluster in silicalite

bound copper pair. The extra-framework Cu^{2+} is clearly visible in the straight channel of the zeolite and is 2.48 Å from the T5-site Cu^{2+}

Finally, we considered the association between a substitutional Cu^{2+} ion and an extra-framework Cu^{+} ion. The Cu^{2+} was substituted for a lattice silicon and an additional Cu^{+} placed in close proximity in silicalite. The energies of six $[Cu^{2+}(Tn), Cu^{+}]$ clusters are given in Table 7. The lowest configuration identified is with copper substituting at the T2 position. The nearest-neighbour Cu–O bond distances are 2.20 and 2.26 Å (2-coordinated) for Cu^{+} extra-framework, compared with 2.66–3.02 Å for Cu^{+} at the lowest energy position in silicalite.

Table 7 Association between Cu^{2+} substituting for Si^{4+} and an extra-framework Cu^{+} ion

Species	Cluster energy/ eV	Binding energy/ eV	Binding energy relative to $[Cu^{2+}(T10), Cu^{+}]$/kJ mol^{-1}
Cu^{+} (extra-framework)	−3.995		
$Cu^{2+}(T2)$	67.997		
$Cu^{2+}(T6) + Cu^{+}$	64.002		
$[Cu^{2+}(T2), Cu^{+}]$	61.281	2.72	0
$[Cu^{2+}(T8), Cu^{+}]$	61.355	2.65	7
$[Cu^{2+}(T19), Cu^{+}]$	61.422	2.58	14
$[Cu^{2+}(T4), Cu^{+}]$	61.465	2.54	18
$[Cu^{2+}(T5), Cu^{+}]$	61.490	2.51	20
$[Cu^{2+}(T11), Cu^{+}]$	61.575	2.43	28

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