Active site configurations within the NO decomposition catalyst, Cu-ZSM-5; the role of framework aluminium

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Computer modelling techniques have been used to identify the extra-framework copper clusters which form the active sites in the Cu-ZSM-5 de-NO$_x$ catalysts. In particular, we suggest that both isolated copper and Cu—OH—Cu species represent useful models for the active site. These species are strongly anchored to the zeolite wall *via* framework aluminium, in the absence of which the clusters undergo significant structural modifications. Specifically, we observe changes both in the Cu—O and Cu—Cu bond distances and also in the coordination numbers of the copper. We suggest that such changes are responsible, in part, for the relationship between the copper loading and Si/Al ratio and the catalytic activity of the material.

Copper, when ion exchanged into the H-ZSM-5 zeolite is found to effectively catalyse the decomposition of NO into N_2 and O_2,[1] a discovery which has stimulated much interest in the application of such ion exchanged zeolites as automobile exhaust catalysts.[2,3] However, the Cu-ZSM-5 system suffers various inadequacies as an automobile catalyst, including thermal instability, narrow operating temperature range, ease of catalyst poisoning and inability to accommodate the varying emissions of hydrocarbons and nitrogen oxides associated with variable engine operation.[4] The design of improved catalysts, which do not suffer these deficiencies, would be greatly assisted by knowledge of the structure and reaction mechanisms in these systems.

In previous work we have identified, using computer simulation techniques, models for the copper containing active sites within the Cu-ZSM-5 system.[5] We propose that the active site comprises both isolated copper species and Cu—OH—Cu clusters which are anchored to the zeolite wall *via* framework aluminium. It has been shown that the turnover frequency for NO decomposition depends on the Si/Al ratio.[6] Furthermore, it has been suggested that the copper containing active sites are located in the vicinity of framework aluminium.[7–9] In this present study we consider the influence of the framework aluminium on the configurations of the copper species within the ZSM-5 zeolite, identified previously, to help elucidate the role of framework aluminium on the active site configurations and hence the catalytic activity.

Potential models and minimisation methods

We have used standard static lattice methods, the methodologies of which are given in more detail elsewhere[10] and are only presented in outline here. The methods are based on the calculation and minimisation of lattice energy of the system using the GULP program.[11] By 'system' we are referring to the zeolite framework and, in this case, additional extra-framework species. During the minimisation the positions of the framework and extra-framework ions are varied. The interatomic potentials used to describe the interactions between the component species of the system include long-range Coulombic terms, two- and three-body, parameterised short-range repulsive potentials, with polarisability of the component species introduced *via* the shell model.[12] In this present study, the parameters for the zeolite are taken from the work of Jackson and Catlow[13] and those for the copper from Sayle *et al.*[5]

Generation of configurations for extra-framework copper species

We consider models appropriate to the active Cu-ZSM-5 system: in particular we concentrate on the system prepared by Iwamoto *et al.*[14] which comprises 7.6 aluminium atoms per unit cell (containing 96 T-sites) and 157% copper loading, where 100% exchange would correspond to one Cu^I ion for each framework aluminium. Assuming equal loading of Cu^I and Cu^{II} as discussed in ref. 15, this composition corresponds to approximately 4 Cu^I and 4 Cu^{II} per 96 silicon T-sites with charge neutrality facilitated *via* the addition of 4 OH^- species. To model this system, trial structures were constructed by replacing, at random, 8 of the 96 T-sites with aluminium ions. The 4 Cu^{II}, 4 Cu^I, 4 OH^- extra-framework species are introduced into the zeolite, again randomly, with the only constraint imposed being a simple proximity criterion to prevent excessive steric overlap; potentially overlapping extra-framework species are rejected and a further random insertion applied. This procedure was repeated to obtain 2000 'trial structures' and the energy of each system calculated. Full energy minimisation

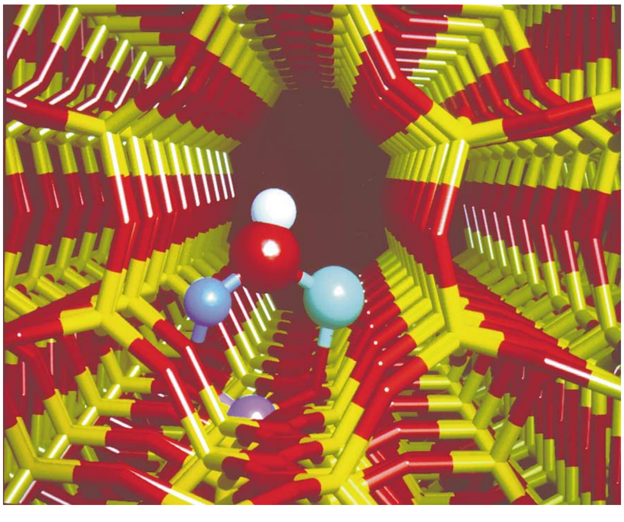

Fig. 1 Illustration of the proposed active site structure within the Cu-ZSM-5 NO decomposition catalyst. Silicon and lattice oxygen are the yellow and red sticks respectively, hydroxyl oxygen is represented by the red sphere, hydrogen is white, aluminium is purple, Cu^{II} and Cu^I are the small and large blue balls respectively.

Table 1 Bond distances, coordination number and association with framework aluminium (if any) for each of the copper ions within each of the six systems where system 1 refers to the most energetically favourable system. The lighter numbers are calculated for the purely siliceous form of the zeolite where all the aluminiums have been replaced, while the bold numbers are for the aluminosilicate

system 1

	Cu—O/Å	Cu—OH/Å	Cu—Cu/Å	Cu—Al/Å	CN
$\mathrm{Cu^{II}}$	2.17, 2.18, 2.29	1.71	3.40		4
	2.02, 2.14, 2.31	**1.72**	**3.29**	**2.88**	**4**
$\mathrm{Cu^{I}}$	2.08, 2.16	1.94			3
	2.07, 2.09	**1.91**			**3**
$\mathrm{Cu^{II}}$	2.05, 2.10, 2.12, 2.29	1.84			5
	2.05, 2.09, 2.14, 2.34	**1.83**			**5**
$\mathrm{Cu^{II}}$	2.09, 2.16	1.85, 1.86	2.86		4
	2.01, 2.28	**1.84, 1.84**	**2.85**	**3.21**	**4**
$\mathrm{Cu^{II}}$	2.14, 2.17	1.83, 1.84			4
	2.01, 2.13	**1.86, 1.87**		**2.93**	**4**
$\mathrm{Cu^{I}}$	2.03, 2.08, 2.09, 2.13				4
	2.01, 2.02, 2.10, 2.16			**2.76**	**4**
$\mathrm{Cu^{I}}$	2.06, 2.10, 2.22, 2.25				4
	2.02, 2.07, 2.10, 2.28			**2.80**	**4**
$\mathrm{Cu^{I}}$	2.03, 2.19, 2.19				3
	2.00, 2.01			**2.76**	**2**
system 2					
$\mathrm{Cu^{II}}$	2.35	1.62, 1.77	3.36		3
		1.62, 1.77	**3.35**		**2**
$\mathrm{Cu^{I}}$	2.12, 2.18, 2.36	1.90			4
	2.08, 2.08	**1.91**			**3**
$\mathrm{Cu^{II}}$	2.09, 2.24, 2.27	1.83, 1.86	2.98		5
	2.03, 2.08	**1.83, 1.84**	**2.82**	**2.91**	**4**
$\mathrm{Cu^{II}}$	2.16, 2.19, 2.30	1.82, 2.22			5
	2.03, 2.06	**1.86, 1.86**		**2.90**	**4**
$\mathrm{Cu^{II}}$	1.98, 1.98, 1.99, 2.21				4
	1.93, 1.94, 2.04, 2.19			**2.91, 3.14**	**4**
$\mathrm{Cu^{I}}$	2.06, 2.07, 2.12, 2.35				4
	1.97, 1.98			**2.71**	**2**
$\mathrm{Cu^{I}}$	1.95, 2.02, 2.13, 2.16				4
	2.00, 2.11, 2.13, 2.15, 2.19			**2.62, 2.90**	**5**
$\mathrm{Cu^{I}}$	2.04, 2.16, 2.17, 2.22, 2.22				5
	2.07, 2.07, 2.14, 2.14, 2.28			**2.58**	**5**
system 3					
$\mathrm{Cu^{II}}$	2.03, 2.06	1.66	3.40		3
	1.82, 2.23	**1.70**	**3.40**	**2.83, 3.35**	**3**
$\mathrm{Cu^{I}}$	2.11	1.96, 2.06			3
	2.19	**1.99, 2.02**			**3**
$\mathrm{Cu^{II}}$	1.82, 2.19				2
	1.82, 1.83			**2.76**	**2**
$\mathrm{Cu^{II}}$	2.12, 2.15	1.63			3
	2.03, 2.05	**1.63**		**2.93**	**3**
$\mathrm{Cu^{II}}$	2.10, 2.11, 2.11	1.68	3.48		4
	1.96, 2.02, 2.18	**1.69**	**3.06**	**2.87**	**4**
$\mathrm{Cu^{I}}$	2.04, 2.14, 2.25	1.95			4
	1.96, 2.09	**1.89**		**2.76**	**3**
$\mathrm{Cu^{I}}$	2.03, 2.05, 2.10				3
	2.02, 2.14, 2.18, 2.23			**2.87**	**4**
$\mathrm{Cu^{I}}$	2.08, 2.08, 2.12, 2.30				4
	1.98, 2.05, 2.07, 2.15			**2.69, 3.21, 3.22**	**4**
system 4					
$\mathrm{Cu^{II}}$	2.17	1.72, 1.78	3.41		3
	1.97	**1.72, 1.79**	**3.32**		**3**
$\mathrm{Cu^{I}}$	2.07, 2.08	1.93			3
	2.09, 2.14	**1.92**			**3**
$\mathrm{Cu^{II}}$	2.18, 2.19, 2.32	1.69	3.16		4
	1.98, 2.00	**1.69**	**3.26**	**2.87**	**3**
$\mathrm{Cu^{I}}$	2.07, 2.10	1.92			3
	2.07, 2.11	**1.91**			**3**
$\mathrm{Cu^{II}}$	2.00, 2.01, 2.04, 2.08, 2.37				5
	1.92, 1.92, 1.97			**2.70, 2.71**	**3**
$\mathrm{Cu^{II}}$	2.13, 2.13, 2.29, 2.30	1.71	3.37		5
	2.11, 2.17, 2.18	**1.74**	**3.40**	**3.38, 3.39, 3.39**	**4**

Table 1 (*continued*)

	Cu—O/Å	Cu—OH/Å	Cu—Cu/Å	Cu—Al/Å	CN
$\mathrm{Cu^{I}}$	2.02, 2.14	1.96			3
	1.94, **2.28**	**1.95**		**2.88**	**3**
$\mathrm{Cu^{I}}$	2.06, 2.06, 2.15				3
	2.08, **2.16**, **2.20**, **2.22**			**2.72**	**4**
system 5					
$\mathrm{Cu^{II}}$	2.02, 2.22	1.73			3
	1.96, **1.97**	**1.66**	**3.44**	**2.85**	**3**
$\mathrm{Cu^{II}}$	2.04, 2.26, 2.37	1.92, 1.93			5
	2.06, **2.14**	**1.74**, **1.83**		**2.88**	**4**
$\mathrm{Cu^{II}}$	2.10, 2.11, 2.13	1.72	3.48		4
	1.94, **2.08**	**1.67**	**3.04**	**2.83**	**3**
$\mathrm{Cu^{I}}$	2.14, 2.16, 2.16	1.93			4
	2.01, **2.05**	**1.95**		**2.77**, **3.31**	**3**
$\mathrm{Cu^{II}}$	2.10, 2.15, 2.22	1.75			4
	2.08, **2.11**	**1.60**		**2.91**	**3**
$\mathrm{Cu^{I}}$	2.09, 2.12, 2.16, 2.21				4
	1.99, **2.02**, **2.03**			**2.64**, **2.95**	**3**
$\mathrm{Cu^{I}}$	2.02, 2.12, 2.18, 2.21				4
	1.99, **2.01**, **2.14**, **2.25**			**3.07**, **3.23**	**4**
$\mathrm{Cu^{I}}$	2.05, 2.12, 2.15, 2.30				4
	1.99, **2.00**, **2.09**, **2.16**			**2.65**, **3.00**	**4**
system 6					
$\mathrm{Cu^{II}}$	2.03, 2.03, 2.13, 2.17				4
	1.90, **1.93**, **2.09**			**2.81**, **2.85**	**3**
$\mathrm{Cu^{II}}$	1.96, 2.11, 2.17				3
	1.94, **2.05**, **2.06**			**2.89**	**3**
$\mathrm{Cu^{II}}$	1.80, 2.21	1.68	3.24		3
	2.09, **2.13**, **2.29**	**1.68**	**3.22**	**3.30**	**4**
$\mathrm{Cu^{I}}$	2.00, 2.06	1.96			3
	2.03, **2.09**	**1.93**		**3.02**	**3**
$\mathrm{Cu^{II}}$	2.18, 2.19, 2.22	1.83			4
	2.02, **2.08**	**1.83**		**3.04**	**3**
$\mathrm{Cu^{I}}$	2.08, 2.13	1.97			3
	2.06, **2.20**, **2.26**, **2.30**	**2.13**		**2.58**, **3.16**	**5**
$\mathrm{Cu^{I}}$	2.04, 2.12				2
	1.99, **2.00**			**2.73**	**2**
$\mathrm{Cu^{I}}$	2.05, 2.09, 2.13, 2.24				4
	1.98, **2.12**, **2.13**			**2.71**	**3**

was then applied to those 20 energetically most stable systems. The procedure should generate all low energy extra-framework copper configurations within these 20 systems. Specifically, the most likely candidates for the active site within Cu-ZSM-5 catalysts comprise copper pairs bridged *via* OH groups[5] which account for 25% of the total copper introduced (see Fig. 1). We also note that these Cu—OH—Cu clusters are anchored *via* one, or more, framework aluminium species. In this work we focus on the role of framework aluminium on the structure of these clusters. To this end we considered the six systems with the lowest energy and replaced all the framework aluminium with silicon; the formal charges assigned to silicon were reduced to accommodate the excess charge. The resulting configuration of the copper species within the purely siliceous form of the zeolite were then compared directly with those identified in the previous study where framework aluminium was included.

Results and Discussion

Bond distances and coordination numbers, which explicitly describe the clusters for each of the six lowest energy systems, are given in Table 1. In each Table the Cu—O, Cu—OH, Cu—Cu and Cu—Al bond distances together with the copper coordination number (CN) are given. Bond distances and coordination numbers, averaged over all the six systems are reported in Table 2 which suggests that when Al is replaced by Si the mean $\mathrm{Cu^{II}}$—O and Cu—Cu distances increase by 0.1 Å together with $\mathrm{Cu^{II}}$ and $\mathrm{Cu^{I}}$ coordination number increases of 0.5 and 0.1 respectively. These observations can be rationalised when one considers the strong association of the framework aluminium with the extra-framework copper species: replacement of a $\mathrm{Si^{4+}}$ with $\mathrm{Al^{3+}}$ results in a net single negative charge located at the T-site. Consequently the interaction between this effectively negatively charged T-site and the +2 charge on $\mathrm{Cu^{II}}$ draws the copper closer to the wall of the zeolite, thus causing a reduction in the average Cu—O distance. The behaviour is greater for $\mathrm{Cu^{II}}$ owing to its larger charge and smaller size compared with $\mathrm{Cu^{I}}$. Displacement of the copper towards the T-site also results in a reduction of the coordination of copper to the framework oxygens, which is perhaps best explained by referring to Fig. 2: the copper ion,

Table 2 Average Cu—O bond distances and coordination numbers for the six systems considered. The numbers in bold are for the aluminosilicate, and the lighter figures are for the same systems after all the framework aluminium species have been replaced with silicon

	Cu—O/Å	Cu—OH/Å	CN
$\mathrm{Cu^{II}}$	2.142	1.790	3.875
	2.045	**1.760**	**3.417**
$\mathrm{Cu^{I}}$	2.125	1.955	3.542
	2.095	**1.958**	**3.417**

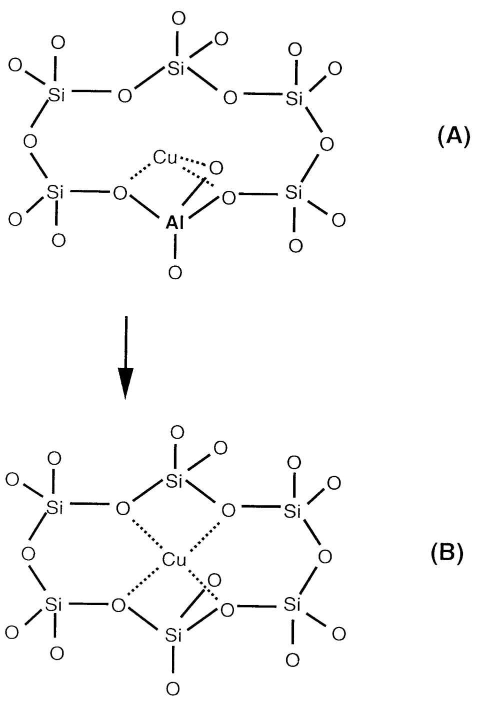

Fig. 2 Representation of the coordination of the extra-framework copper species to lattice oxygens in the MFI zeolite with and without aluminium at the T-site: (A) aluminium accommodates a silicon T-site and the strong association between the aluminium and the copper facilitates a displacement of the copper toward the aluminium. In this case the copper has a coordination number of three. Subsequent replacement of this aluminium with silicon (B) eliminates any association and the coordination number increases to four. This example is hypothetical to illustrate the reduction in coordination of extra-framework copper species when associated with framework aluminium.

initially associated with a framework aluminium, has a coordination number of three. Replacing this aluminium with silicon enables the copper to adopt a four fold coordination as there is now no displacement of the copper ion towards the framework aluminium. For Cu^I the association is weaker and therefore the change in coordination is necessarily smaller (0.1 compared with 0.5).

We now consider these structural changes in closer detail by considering individual cases. First we consider the most stable system (Table 1, system 1). We observe changes in $Cu^{II}-O$ distances of up to 0.18 Å and slight changes in the relative configurations of the extra-framework species but the removal of the framework aluminium has little effect on the overall configuration of the clusters within this system. For the second system (Table 1) there is a notable difference when the framework aluminium is removed: one particular copper cluster conforming to a 'square planar' $Cu_2(OH)_2$ type arrangement is observed to move 2 Å to an alternative location within the zeolite. The displacement of this cluster introduces a slight perturbation of the square planar type configuration characterised by changes in the Cu—Cu and $Cu^{II}-OH$ bond distances which increase by 0.16 Å and 0.36 Å respectively. We note that the coordination of the two Cu^{II} species increases from four to five.

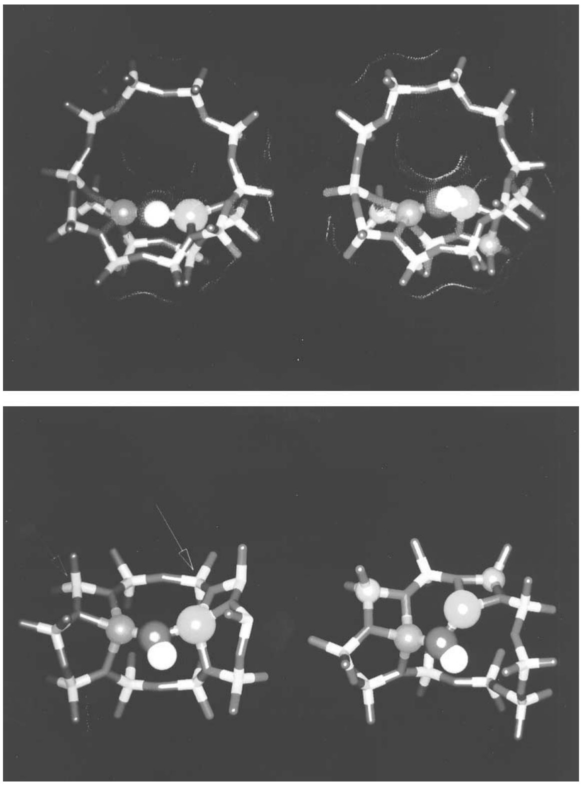

Fig. 3 Representation of a hydroxy-bridged copper pair in the MFI zeolite. To the left of the figure the Al^{3+} have been replaced with Si^{4+}. In the bottom figure part of the zeolite framework has been removed for clarity. The behaviour is more clearly illustrated in Fig. 4. Silicon and lattice oxygen are represented by light and dark sticks respectively, the hydroxy species is represented by overlapping dark (oxygen) and light (hydrogen) spheres and Cu^{II} and Cu^I are represented by small and large spheres respectively.

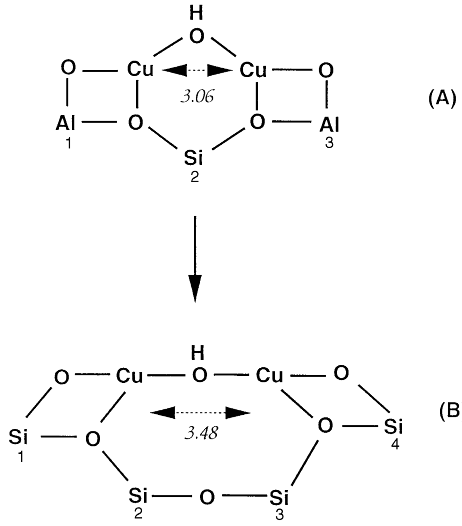

Fig. 4 (A) Illustration of the $Cu^I-OH-Cu^{II}$ cluster associated with two framework aluminiums (see Fig. 3) and (B) the same Cu–OH–Cu cluster when the two framework aluminium species have been replaced with silicon.

In the third system considered (Table 1), the two copper species in the second $Cu^{II}-OH-Cu^I$ cluster are each anchored by framework aluminium (Fig. 3 and 4) and form part of a six-membered ring with the zeolite framework. Replacing the aluminium with silicon eliminates the strong anchoring of the cluster to the zeolite wall at these T-sites and the Cu—Cu repulsion causes the $Cu^{II}-OH-Cu^I$ to bridge across to the next silicon site resulting in an eight-membered ring with the Cu—Cu distance increasing by 0.42 Å from 3.06 Å to 3.48 Å. We note that Cu—Cu bond distances of 3.0 Å have been observed in the active catalyst.[16] A similar observation occurs in system 5 (Table 1). In this case the two copper species are both anchored to a single aluminium to form a six-membered ring. This is perhaps a more likely scenario since the probability of two neighbouring framework aluminiums within a system of high Si/Al ratio is low. The replacement of this aluminium with silicon results in the $Cu^{II}-OH-Cu^I$ bridging across two silicon

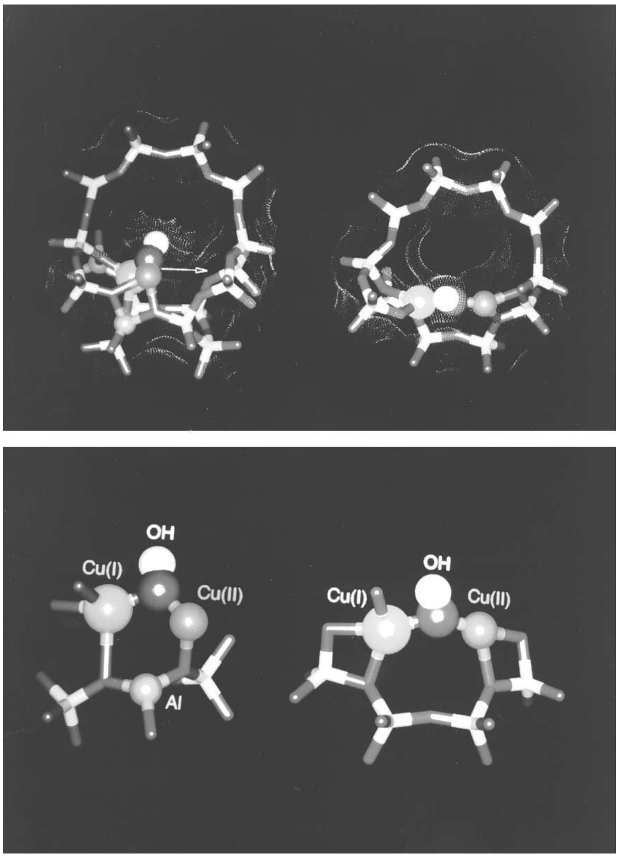

Fig. 5 Representation of a $Cu^{II}-OH-Cu^{I}$ cluster bridging across a single framework aluminium. To the right of the figure the same cluster is shown but with the Al^{3+} replaced with Si^{4+}. The Cu–Cu repulsion causes the cluster to bridge across to an adjacent site. In the bottom figure part of the zeolite framework has been removed for clarity. Notation is as in Fig. 3.

T-sites to form an eight-membered ring (Fig. 5) and consequently the Cu—Cu distance increases from 3.04 Å to 3.48 Å.

Discussion and Conclusions

The replacement of framework aluminium with silicon within the Cu-ZSM-5 system results in significant modifications of the configurations of the copper species. In particular, the copper pairs, bridged with extra-framework OH, sustain large changes in both the Cu—O and Cu—Cu bond distances and also in the coordination number of the copper. Moreover, we have suggested that these Cu—OH—Cu species represent useful models for the active site and changes in their configurations are likely to influence the catalysis. Such changes can be introduced for example by increasing the Si/Al ratio which would result in less clusters associated with a framework aluminium. In addition, increasing the copper loading would again reduce the number of clusters associated with framework aluminium. Indeed, the Si/Al ratio and/or copper loading have been linked to the turnover frequency of NO decomposition, for example see ref. 6. We therefore suggest that the changes in catalysis with changes in the Si/Al ratio and/or copper loading may be attributed, in part, to the subtle modifications of the copper species within the system as a result of the strong association between the framework aluminium and extra-framework copper.

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