Electronic Supplementary Material (ESI) for Nanoscale.

# Supporting Information for Assessing relative stability of copper oxide clusters as active sites of CuMOR zeolite for methane to methanol conversion: size matters?

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## S.1 Location of copper atoms in SSZ-13

The results on the aluminium loading agree with the data on the influence of Al on the position of copper species in the SSZ-13 zeolite. There, $Cu^{2+}$ and $CuOH^+$ species prefer to be located in the middle of the pore in the presence of two symetrically arranged Al atoms, while for purely Si pore or a pore with only a single Si atom substituted with Al the copper species tends to bind to one or two oxygens of the pore (S1). If this understanding is correct, then Al loading might be used to adjust the level of interaction between the Cu–O cluster and the pore, and, possibly, to preferentially form a certain type of cluster.

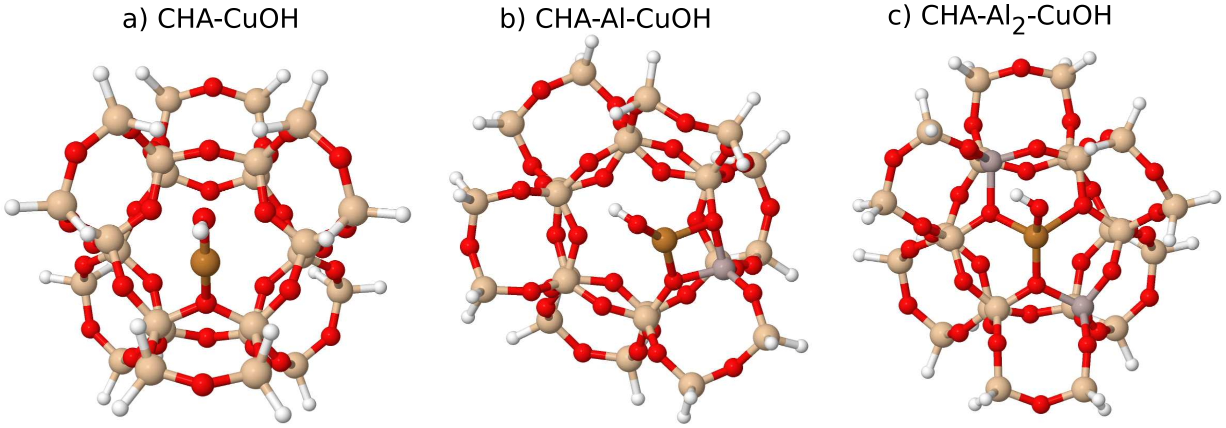

Figure S1: Locally optimized structures of CuOH adsorbed on a six-member ring pore of CHA (SSZ-13) with (a) no Al atoms, (b) one Al atom, (c) two Al atoms.

## S.2 Formal charge balance in copper oxide clusters

One of the important aspects of the copper oxide clusters formation is the charge balance in the exchanged zeolite system. Assuming the neutrality of the zeolite and two aluminium atoms per pore, one ends up with the necessity of compensating the negative "$-2$" charge of the zeolite with the copper oxide cluster. In the simplest mono($\mu$-oxo)dicopper case, the application of a formal charge view is straightforward, and, as widely used in literature,[1] assumes the Cu(II) species:

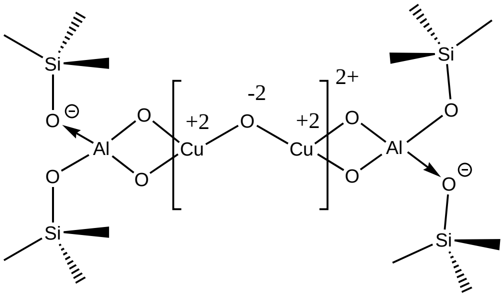

Figure S2: Formal assignment of the oxidation states in the case of the mono($\mu$-oxo)dicopper site.

Already for the case of bis($\mu$-oxo)dicopper site the formal charge assignment becomes more tricky. In order to keep the overall "+2" charge of the cluster one needs to either assume the existence of Cu(III) species, or a peroxo- center:[2]

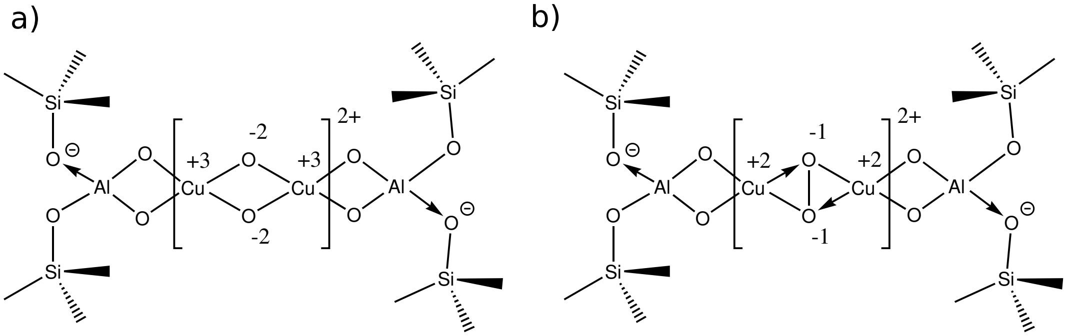

Figure S3: Formal assignment of the oxidation states in the case of the bis($\mu$-oxo)dicopper site, assuming (a) the existence of Cu(III) species, or (b) the formation of a peroxo- species.

In the case of the $Cu_3O_3$ trimer structure, Pidko and Lercher suggested several possible resonance structures to describe the formal charge configuration of the copper oxide species, assuming the possibility of co-existence of different oxidation states of copper or oxygen in the same structure.[3] However, such a picture is obviously much more complicated compared to the simple formal Cu(II)/O(−II) charge balance considerations. Following both ideas, one can thus, in principle, suggest two homologue series of copper oxide clusters, the one corresponding to the $Cu_nO_n{}^{2+}$ composition with the "tricky" oxidation states of copper and/or oxygen ($Cu_2O_2{}^{2+}$, $Cu_3O_3{}^{2+}$, $Cu_4O_4{}^{2+}$, $Cu_5O_5{}^{2+}$), and the one corresponding to the perfectly stoichiometrical $Cu_nO_{n-1}{}^{2+}$ composition ($Cu_2O^{2+}$, $Cu_3O_2{}^{2+}$, $Cu_4O_3{}^{2+}$, $Cu_5O_4{}^{2+}$).

## S.3 Selected isomers of the $\mathrm{Cu}_n\mathrm{O}_{n-1}{}^{2+}$ stoichiometry

Figure S4 compares three lowest-lying isomers identified by the global geometry optimization for the $\mathrm{Cu_3O_2}{}^{2+}$, $\mathrm{Cu_4O_3}{}^{2+}$, and $\mathrm{Cu_5O_4}{}^{2+}$ clusters.

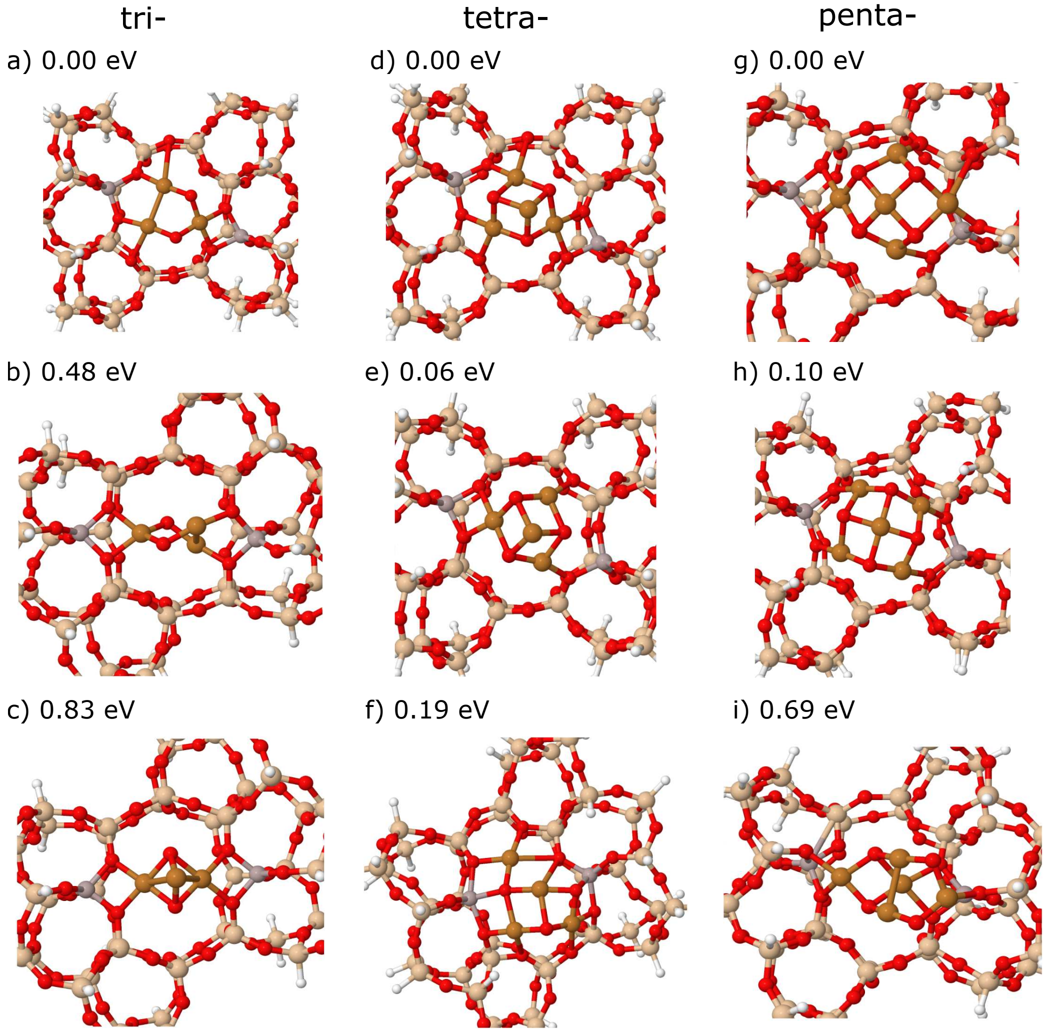

Figure S4: Ground-state structures and first two lowest-lying isomers of (a–c) $\mathrm{Cu_3O_2}{}^{2+}$, (d–f) $\mathrm{Cu_4O_3}{}^{2+}$, and (g–i) $\mathrm{Cu_5O_4}{}^{2+}$.

## S.4 Influence of the spin state on cluster stability

The all-electron code used in our work is especially well suited for correct description of the spin manifold of the transition metals due to the employed numeric atom-centered orbitals.[4] Furthermore, FHI-aims allows an automated optimization of spin-polarized systems through collinear (scalar) spin-DFT formalism. In this case, each geometry optimization is, therefore, effectively coupled with the spin state optimization, and all geometries and energies reported herein correspond to the optimal spin state for each system. Identified optimal spin states of mordenite structures are summarized in the table below.

Table S1: Optimized spin states of different copper oxide clusters in the 8-ring channel of mordenite.

| Cu site | Relative stability per CuO, eV | |
|---|---|---|
| | ${Cu_nO_n}^{2+}$ | ${Cu_nO_{n-1}}^{2+}$ |
| dicopper | singlet | singlet |
| tricopper | doublet | doublet |
| tetracopper | singlet | triplet |
| pentacopper | doublet | doublet |

## S.5 Synthesis of the copper-exchanged mordenite

The typical mordenite synthesis procedure assumed in our group adapts the method of Jongkind *et al.*, which utilizes a cyclic amine, hexamethyleneimine (HMI), as a structure directing agent.[5] Mordenite was obtained from a gel with the following molar composition: $SiO_2 : Al_2O_3 : Na_2O : HMI : H_2O = 30 : 2 : 7.3 : 11.4 : 636$. A slurry is prepared by initially mixing sodium hydroxide pellets (Fischer, 98 wt.%) with water. Two-thirds of the NaOH solution is added dropwise to fumed silica (Sigma-Aldrich, 99.8 wt.%) and stirred until the silica is dissolved. The HMI (Aldrich, 99 wt.%) was then added to the silica/NaOH slurry. Aluminum sulfate octadecahydrate (Aldrich, 98 wt.%) is added to the remaining one-third of the NaOH solution. The two solutions were combined and mixed for 1 hour. The slurry (pH = 12.3) is transferred to a Teflon-lined stainless steel autoclave and placed in the oven at 165°C for 90–160 hours. The solid products are washed and dried overnight. X-day diffraction patterns were collected with a Panalytical X'Pert PRO-MPD, using Cu K$\alpha$ radiation. Chemical analysis is performed with a Varian SpectrAA 220 FS spectrometer. Pure mordenite is obtained after 90 hr. of hydrothermal treatment. The chemical composition, obtained from AAS, corresponds to a Si/Al ratio of 13.3, which is equivalent to 3.4 Al per unit cell.

## References

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