Design, implementation and production upscaling of novel, high-performance, cluster-based catalysts for CO_2 hydrogenation

Deliverable D.4.1

Mass spectra of metal-oxide clusters

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Goal.

The goal of this deliverable is to provide the first mass spectra of copper (Cu) oxide (O) clusters with different copper/oxygen ratio to demonstrate the ability to prepare such clusters. Furthermore, these mass spectra provide important insight into the size and composition range that can be produced and thus, provides the basis for all further reactivity experiments.

Approach and Experimental Details.

We have used a laser ablation source to produce the cationic copper oxide clusters. In this source the clusters were produced by pulsed laser ablation of a rotating copper target using the second harmonic of a Nd:YAG laser. The ablation took place in a 3 mm diameter and 60 mm long growth channel in the presence of a short pulse of helium carrier gas seeded with about 1% oxygen. The cluster-helium mixture was then expanded into vacuum, forming a molecular beam, before being mass analyzed with a pulsed reflectron time-of-flight mass spectrometer and detected with a microchannel plate detector. To optimize cluster production with different size and composition different experimental conditions have been varied (such as e.g. the oxygen content in the He carrier gas or the time between the He pulse and laser ablation and the time between laser ablation and extraction in the time-of-flight mass spectrometer).

Results.

Figure 1 and Figure 2 show the first mass spectra of copper oxide clusters produced by laser ablation of a copper target in the presence of about 1%O_2/He. For the detection of the mass spectrum displayed in Figure 1 the experiment was optimized for the production of rather small clusters with up to four copper atoms, whereas for the detection of the mass spectrum displayed in Figure 2 the experiment was optimized for the production of larger clusters. It should be noted that copper has two stable isotopes (^{63} Cu and ^{65}Cu with natural abundances of about 69% and 31%, respectively) which leads to several peaks in the mass spectrum corresponding to one cluster stoichiometry. In the figures we have only labeled the first peak of each isotope distribution although this is not necessarily the mass peak of the highest intensity. Potential problems arising from the cluster isotope distributions (e.g. low cluster intensity for larger clusters, mass overlap in reactivity experiments, etc.) might in the future be solved by using an isotopically enriched sputter target. Close inspection of the mass spectra leads to the following conclusions:

- The production of copper oxide clusters in the size range of one to eight copper atoms is possible.
- The oxygen content in the clusters strongly depends on the amount of Cu atoms and is rather independent of the oxygen content in the carrier gas. A reduction of the latter to 0.5%O_2/He and 0.25%/He leads to a reduction of the amount of formed clusters but does not change the cluster distribution.
- Clusters containing the same number of Cu atoms but different numbers of oxygen atoms show a non-trivial intensity pattern indicating the particular stability/instability of specific $Cu_xO_y^+$ compositions. This is expected to strongly influence the reactivity of the clusters, which will be probed in a later phase.

- For the smallest clusters CuO_y^+ and $Cu_2O_y^+$ the oxygen content can be varied in a large range from zero to six atoms. In contrast, clusters containing a larger number of Cu atoms tend to incorporate also a larger amount of oxygen.

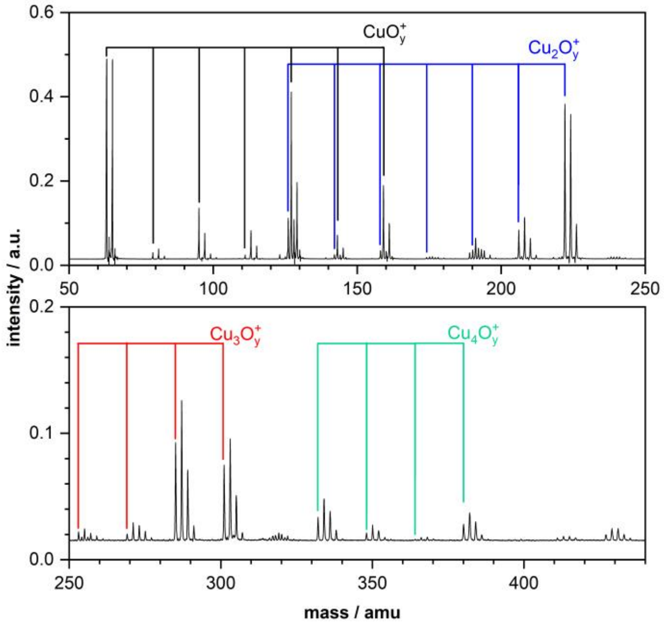

Figure 1: Mass spectrum of copper oxide clusters obtained by laser ablation of a copper target in the presence of 1% O_2/He. The cluster production and detection was optimized for the production of small clusters with up to 4 copper atoms. The labeled peaks correspond to the cluster stoichiometries CuO_y^+ (y = 0-6; black), $Cu_2O_y^+$ (y = 0-6; blue), $Cu_3O_y^+$ (y = 4-7; red), and $Cu_4O_y^+$ (y = 4-7; green).

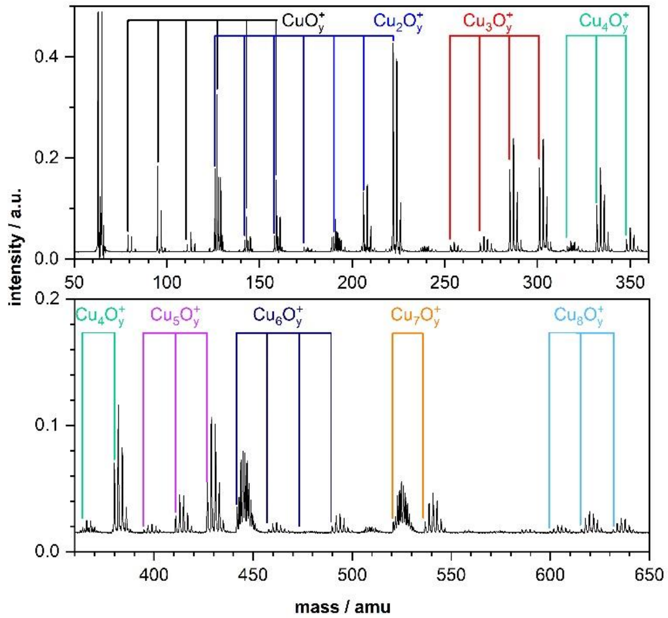

Figure 2: Mass spectrum of copper oxide clusters obtained by laser ablation of a copper target in the presence of 1% O_2/He. The cluster production and detection was optimized for the production of larger clusters with up to 8 copper atoms. The labeled peaks correspond to the cluster stoichiometries CuO_y^+ (y = 1-6; black), $Cu_2O_y^+$ (y = 0-6; blue), $Cu_3O_y^+$ (y = 4-7; red), $Cu_4O_y^+$ (y = 4-8; green), $Cu_5O_y^+$ (y = 5-7; purple), $Cu_6O_y^+$ (y = 4-7; olive), $Cu_7O_y^+$ (y = 5,6; orange), and $Cu_8O_y^+$ (y = 6-8; light blue).

Conclusions.

We have produced for the first time series of copper oxide clusters in the size range of one to eight copper atoms and different copper/oxygen ratio. These experiments will provide the basis of all future reactivity experiments and are also meant to guide the theoretical exploration of cluster structures and cluster reactivity. In particular, the work of ESR 3 (UU) during his secondment at FETI will be based on these experiments.