Reactivity of Cu Single Atoms and Mass-Selected Nanoparticles Correlated with their CO Electroreduction Activity

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Introduction
Nanoparticle catalysts are desirable because of the high mass-to-surface area ratio. Mass-selected nanoparticles are used as a model system to determine size effects in catalysis, if any. With our setup, we can produce well-characterized mass-selected nanoparticles. CO-TPD has previously been done on for example Pt nanoparticles to correlate activity and reactivity to explain a size effect in catalysis.[1] Cu is well-known to be unique among the pure metals in its wide selectivity in hydrogenation of CO$_2$ to multi-carbon products. Isolating the active sites and corresponding reaction mechanisms is difficult. The CO binding energy is used as a descriptor for the reactivity in CO$_2$RR, so CO-TPD would be an ideal characterization technique to probe the actual reactivity of a sample (in UHV). These features on Cu start showing near the temperature of liquid nitrogen, so modifications needed to be made. To this end, a module has been designed to allow for CO-TPD on Cu samples.[1] Perez-Alonso, F. J., McCarthy, D. N., Nierhoff, A., Hernandez-Fernandez, P., Strebelt, C., Stephens, I. E. L., Nielsen, J. H. and Chorkendorff, I. (2012). Angew. Chem. Int. Ed., 51: 4641–4643. doi:10.1002/anie.201200586

Mass-selected nanoparticles

Custom-made TPD stage
A device was designed to allow for CO-TPDs on Cu within the same vacuum system as samples are prepared in. Simulations in COMSOL were used to identify and optimize plausible designs.

- Cooling
  - Flow of LN$_2$ through hollow Cu cylinder
  - Contact area of sample: 36 %

- Heating
  - W filament (150 W/15 V)
  - 12 V power supply
  - Floating at 2.9 kV (negative)
  - Deflector cup under filament

- Temperature control
  - Type K thermocouple integrated on sampleholder
  - Contacts to measure sample surface temperature

- Detection
  - QMS with Sniffer

Characterization
In combination with UHV synthesis of mass-selected nanoparticles, a range of techniques is available for characterization without exposure to air.

- XPS
- ISS
- SEM
- AES
- SAM
- STM
- TEM

These techniques give a lot of information about prepared samples, but not about the reactivity of the surface explicitly.

Measurements

Figure 1: CO-TPD on oxide-derived copper showing a high temperature feature not explained by diffusion effects. From [2].

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Figure 2: Polycrystalline copper reference sample. Mass 30 signal. Heating rate 0.5 K/s. Red, green, and purple are consecutive scans for reproducibility. Blue scan, no CO was dosed.

Figure 3: Nanoparticle sample. Mass 30 signal. 20% coverage 5 nm Cu on glassy carbon. Heating rate 0.5 K/s. Black, red, green are first scan, second scan and blank, respectively.

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