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In situ S/TEM Reduction Reaction of Calcined Cu/BEA-zeolite Catalyst

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Zeolite-catalyzed processes represent promising approaches to convert C_1 species (e.g., methanol, dimethyl ether (DME)) from syngas into targeted classes of high-value fuels and chemicals. H-BEA, large pore acidic zeolites, can be used to convert methanol and/or DME to branched C_4–C_7 alkanes with high selectivity to isobutane and 2,2,3-Trimethylbutane [1,2]. Recent research has demonstrated that the addition of Cu to the BEA zeolite catalyst can further improve hydrocarbon productivity by incorporation of co-fed H_2 into the desired products [3]. Advanced catalyst synthesis coupled with advanced characterization are key to advancing catalyst research and development; thus, to better understand the mechanism of Cu species incorporation into the BEA zeolite, high-resolution and *in situ* scanning transmission electron microscopy (S/TEM) are being used to provide insight.

In situ closed gas cell microscopy can be utilized to study a range of material systems in response to temperature and reactant gases. *In situ* STEM allow for exposures of catalysts at temperatures up to 1000°C and pressures up to 1atm [4]. In the present work, *in situ* microscopy exposure of the Cu/BEA catalysts in air at 300°C will be correlated with results from similar experiments performed using an *ex situ* lab-scale reactor system (results not included here). The Cu/BEA catalysts were prepared by an incipient wetness method by adding $Cu(NO_3)_2{\cdot}2.5H_2O$ to ammonium beta zeolite (NH_4-BEA) powder with SiO_2/Al_2O_3 ratio of 27 [5]. The actual Cu loading was measured to be 4.3 wt.%. The Cu/BEA catalyst was activated in flowing air (10% O_2/Ar) heated at 2 °C/min to 500°C and held for 5h (calcined Cu/BEA), which was the final material used for the *in situ* S/TEM experiments.

The calcined Cu/BEA particles were mixed in hexane in air and crushed to fit in the 5 μm gas-flow gap of the cell [4]. A droplet of the suspension was placed on the silicon nitride window of a Protochips™ E-chip heater chip. A Protochip Atmosphere™ gas reaction holder was used for the *in situ* STEM experiments, which were conducted using an aberration-corrected JEOL 2200FS operated at 200kV. The gas-cell was flushed three times with nitrogen at 50 Torr to ensure there was no O_2 present in the system. The pressure was then set to 720 Torr, the gas-cell was filled with 4%H_2/Ar, and the temperature was ramped up at a rate of 30°C/min. (0.5°C/sec) from RT to 300°C under flowing 4%H_2/Ar. No significant change in the morphology of the catalyst particles was observed while the temperature was increasing; however, fine-scale precipitates were clearly observed after holding the catalyst for 14 min. at 300°C (Figure 2) and their size increased with further exposure time (2h total) at 300°C. Energy dispersive X-ray spectroscopy (EDS) elemental analysis after exposure in 4%H_2/Ar for 2h at 300°C confirmed that the precipitation observed was primarily associated with Cu. Changes in the Al distribution was also observed. These initial observations suggest segregation of Al into small culsters in addition to Cu-rich precipitate formation, which requires further confirmation. The *in situ* S/TEM results agree with lab-scale experiments [3]. The validation of *in situ* S/TEM capabilities can enable future identification of active sites and catalyst regeneration procedures [5].

References:

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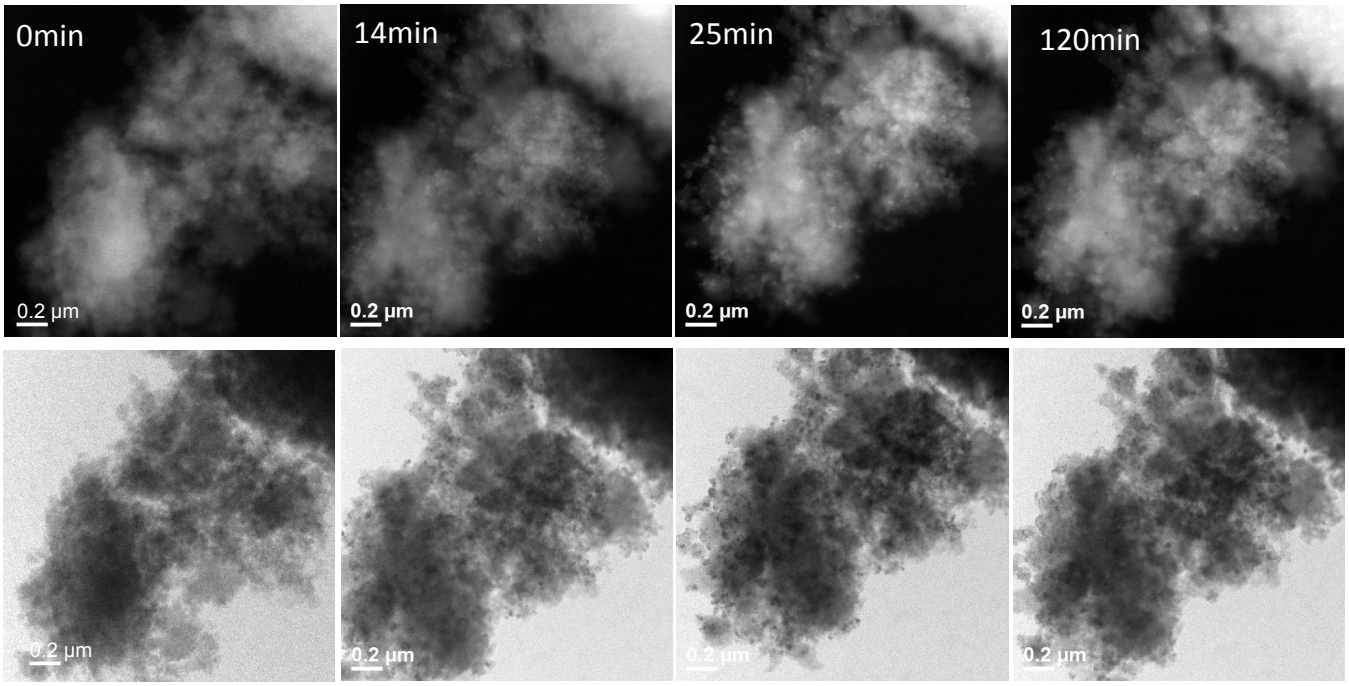

Figure 1. Time-lapsed (zero to 120min.) HAADF-STEM and simultaneously acquired BF-STEM images showing redation behavior of calcined Cu/BEA at 300°C in flowing 4%H_2/Ar, 720 Torr.

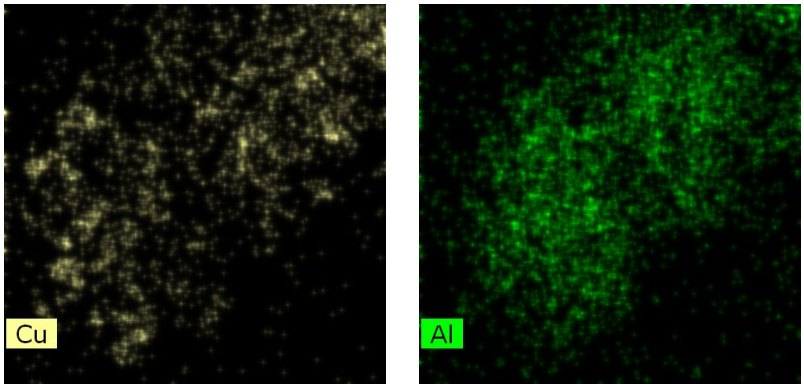

Figure 2. Cu and Al elemental maps for the Cu/BEA particle shown in Figure 1 at 300°C in flowing 4H_2/Ar and 720 Torr after reaching 120min. of *in situ* S/TEM reduction reaction.

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