

## Beamline report: CH-5579

### *In-situ EXAFS spectroscopic investigation of isolated copper aluminate sites on silica / alumina for the selective conversion of methane to methanol*

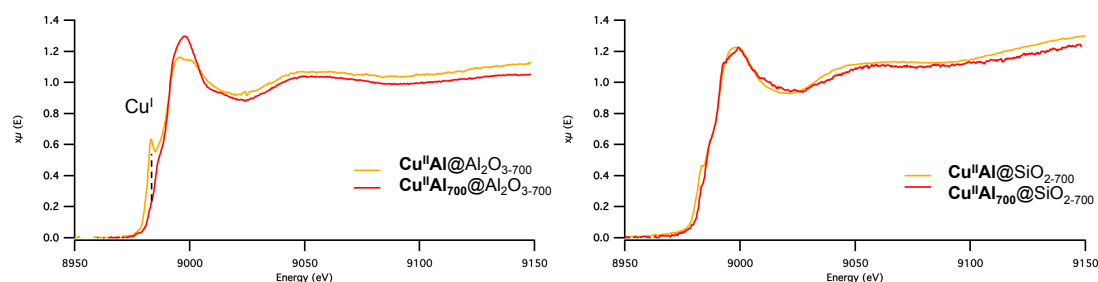
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The experiment carried out during this beamtime involved the study of copper isolated on oxide support (silica or alumina) prepared via surface organometallic chemistry (SOMC) approach, generating a variety of Cu species with different Al/Si environment. The prepared materials were assessed ex-situ (1) after grafting and (2) after thermal activation under synthetic air, by collecting XANES and EXAFS using 1 mm capillaries flamed sealed under inert atmosphere. The low copper contents of the materials ( $\approx 0.5$  wt% Cu) required the use of the fluorescence detector to be able to probe the chemical environment around the copper centers to the second coordination sphere. For the in-situ samples, the thermally activated material was placed in a 3 mm capillary cell using the ESRF glovebox to prevent the exposure of the material to moisture and oxygen; the in-situ reaction was performed with purified gas feed to examine the reactivity of the material and reduction of the copper centers upon reaction with methane. The measurements performed on the studied samples were successful and resulted in high quality data for both the ex-situ and in-situ samples.

In this report, the spectra for two sets of samples are discussed, where the chosen samples correspond boundary cases that exhibit the most significant differences in the coordination spheres of the Cu centers and in their reactivity with methane. The materials were prepared starting with a copper aluminate molecular precursor ( $\text{Cu}^{\text{II}}\text{Al}$ ) grafted on partially dehydroxylated silica ( $\text{SiO}_{2-700}$ ) and alumina ( $\text{Al}_2\text{O}_{3-700}$ ) with similar loading (0.5 wt% Cu); these grafted materials were then thermally activated by treating under dry synthetic air at 700 °C for 12 h.

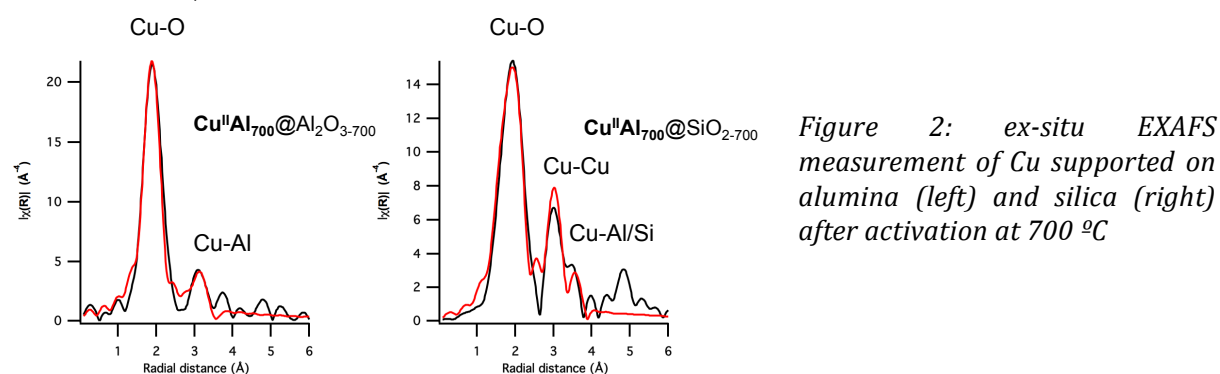
Ex-situ XANES analysis of the grafted materials illustrated significant differences between the two supports ( $\text{Cu}^{\text{II}}\text{Al@Al}_2\text{O}_3$  or  $\text{SiO}_2$ ). Specifically, on alumina, the partial reduction of the  $\text{Cu}^{2+}$  centers is demonstrated by the appearance of the pre-edge feature at 8981 eV, indicating the presence of  $\text{Cu}^+$  in the grafted material (*figure 1, left*). This feature is notably much less prominent in the silica-based material (*figure 1, right*). After thermal activation, both XANES spectra indicates the solely presence of  $\text{Cu}^{2+}$  ion in the material (*figure 1*).



*Figure 1: XANES spectra of  $\text{Cu}^{\text{II}}\text{Al}$  grafted (yellow) and activated (red) on alumina (left) and silica (right)*

The activated material by EXAFS analysis on the ex-situ sample shows similar first shell coordination, dominated by Cu-O scattering. The major difference is observed at higher shell where for the alumina-supported material (*figure 2, left*), it is dominated by the Cu-Al scattering. In contrast, the silica-supported material displays a more complex feature. The scattering at greater radial distance indicates the clustering of the Cu center into small  $[\text{CuO}]_n$  clusters (*figure 2, right*). Based on these data, it was

concluded that alumina facilitates better dispersion of the metal centers, forming monomeric Cu, in contrast to silica where clusters were formed.



In-situ reaction of the thermally activated materials with methane at 200°C, 6 bars for 30 min, show clear changes in the XANES region, reflecting the reduction of the copper centers responsible for the partial oxidation to methanol. The amount of reduced Cu was compared to the methanol production obtained experimentally under similar conditions by using linear combination between the oxidized sample and the reduced sample in-situ under  $\text{CH}_4$  at 500 °C for the alumina material (figure 3, left). For the alumina-based material, this quantification was possible due to the formation of  $\text{Cu}^+$  species after reduction; in contrast, the silica-supported material presented greater reduction to a mixture of  $\text{Cu}^+$  and  $\text{Cu}^0$  (figure 3, right), rendering this analysis impossible. These spectra suggest the greater reducibility of the Cu ions when supported on silica compared to alumina, potentially due to the higher mobility of the ion on the support under the studied conditions.

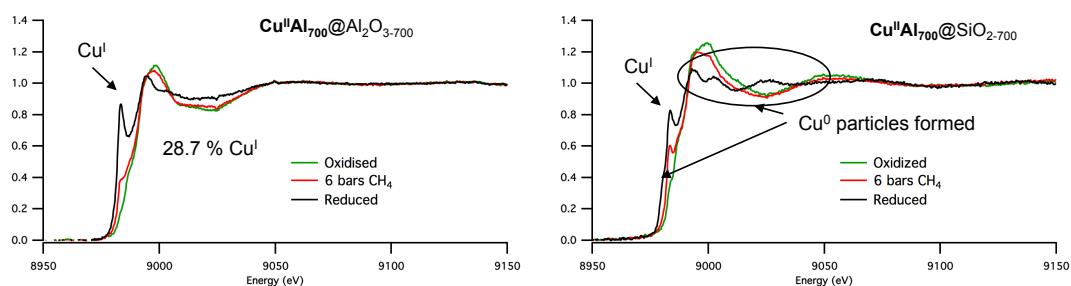


figure 3: In-situ reaction on alumina (left) and silica (right) of the oxidized material (green) the reacted material with methane (red) and the reduced sample (black)