The formation, location and stability of copper nanoparticles formed during the reduction of a copper silicate

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Introduction
Two of the main industrial routes to synthesize supported metal catalysts are incipient wetness impregnation and co-precipitation followed by calcination and reduction. It is unclear, however, how metallic particles form during the reduction of a co-precipitated sample and which of the two routes leads to a more thermally stable catalyst. To study this, we investigated the formation, location and stability of copper particles on silica, synthesized via co-precipitation and incipient wetness impregnation.

Materials and Methods
Copper on silica catalysts were synthesized via incipient wetness impregnation with copper nitrate followed by drying, calcination and reduction, and via reduction of a co-precipitated copper silicate [1, 2]. The formation of an ensemble of metallic copper particles during reduction of the copper silicate was imaged in real time with in-situ TEM. The number, size and location of the emerging copper nanoparticles were tracked over time. For both catalysts, the 3D location of the copper particles after reduction with respect to the silica support was determined with electron tomography. The stability of the copper catalysts was investigated in the methanol synthesis reaction at 40 bars at 260°C for 10 days.

Results and Discussion
In-situ TEM showed that copper particles forming during the reduction of a co-precipitated copper silicate were not mobile, indicating that growth occurred via diffusion of copper species to the nucleated particles (Figure 1). As soon as a new particle appeared it grew first very fast and then slower, expected as the copper ion concentration in the surrounding copper silicate was gradually depleted. As a result, particles that nucleated early during reduction grew, on average, larger than particles that nucleated later.

Electron tomography revealed the 3D location of the copper particles with respect to the silica support (Figure 2). After reduction of the copper silicate, the particles were partially entrapped in the silica, since the copper particles and the silica support were formed at the same time. For copper on silicate, prepared via incipient wetness impregnation of an existing support, the copper particles were located on the surface of the silica.

Copper on silica, prepared via reduction of a co-precipitated copper silicate, showed an improved stability in the methanol synthesis reaction compared to copper on silica prepared via incipient wetness impregnation. Both catalysts had similar initial particle size distributions and particle-particle distances. The main difference between the two catalysts was the location of the copper particles with respect to the support. It is therefore concluded that partial entrapment of the copper particles, originating during the reduction of a co-precipitated copper silicate, resulted in a higher thermal stability of the final copper on silica catalyst.

Significance
Our work showed that supported metal catalysts prepared via co-precipitation may be more stable than prepared via incipient wetness impregnation, since the metallic particles can get partially entrapped in the support during reduction of a co-precipitate.

Figure 1. in-situ TEM images (170 x 170 nm) taken of the same location during reduction of a co-precipitated copper silicate.

Figure 2. TEM tomogram sections of copper on silica prepared via co-precipitation followed by reduction (A) and via incipient wetness impregnation of copper nitrate (B).

References