Scanning Transmission Electron Microscopy for probing the microstructure of bifunctional CuZnAl/ZSM-5 catalysts

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Aberration corrected scanning transmission electron microscopy (STEM) in two and three dimensions in combination with EDS were used to explore the microstructural evolution of CuO-ZnO-Al2O3 (CZA) catalysts onto hierarchical ZSM-5 zeolites during the direct synthesis of dimethyl ether (DME) from syngas. The STEM based approach advanced allowed one to elucidate the distribution of the copper active phase as against the support and to establish the impact of a reactive milieu on the microstructure of the CZA-ZSM-5 catalyst. Upon reaction, the copper distribution evolves from nanoparticles (NPs) to agglomerates located preferentially on the Zn and Al rich grains. The ZSM-5 edges are marked by the presence of NPs before reaction, whereas after reaction a thin copper-rich layer embeds locally the grains. Catalytic experiments have shown that the main factor accelerating deactivation of the catalyst is water formed during reaction. Water addition in the reaction conditions leads to almost full deactivation of the catalyst. In terms of microstructure, apart from the nanoparticles on the ZnO-Al2O3, the active copper (mean particle size of 2 nm) spreads uniformly on the outer surface of the ZSM-5 after the water treatment. In these circumstances, water significantly accelerates migration and segregation of Cu in the catalyst. The STEM tomography corroborated with STEM–EDS analysis and mapping identified the role of different treatments on the catalyst microstructure.