

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

Simona Moldovan^{1*}, Mengdie Cai², Georgian Melinte¹, Vijayanand Subramanian², Ana Palcic³, Valentin Valtchev³, Vitaly V. Ordonsky², Andrei Y. Khodakov², and Ovidiu Ersen¹

¹ IPCMS, Université de Strasbourg, 23, rue du Loess BP 43, F-67034 Strasbourg, France

² UCCS, Université Lille 1-ENSCL-EC Lille, Bat. C3, Cité Scientifique, 59655 Villeneuve d'Ascq, France

³ LCS, ENSICAEN, 6 Boulevard Maréchal Juin, 14000 Caen, France

*simona.moldovan@ipcms.unistra.fr; Téléphone : +33 (0)3 88 10 71 04; Fax : +33 (0)3 88 10 72 48

1. INTRODUCTION

We are assisting nowadays at the continuous development of alternative energy sources in the general context of oil resource diminishing whilst the economical demands are fastly growing. Dimethyl ether (DME) is considered an appropriate alternative to diesel fuel because of high cetane number, low auto-ignition temperature and reduced emission contaminants. In direct DME synthesis, carbon monoxide conversion occurs in a single reactor, over a bifunctional catalyst, which ideally combines the methanol synthesis and dehydration catalyst characteristics. The methanol synthesis requirement is fulfilled by copper (Cu) metal nanoparticles as active phases associated with a promoter i.e. the zinc (Zn), whereas the dehydration criterion demands for an acid catalyst, such as the ZSM-5 successfully tested [1]. Obviously during the reaction, the catalysts are exposed to more or less aggressive conditions, which are ones of the main inputs for the DME synthesis. In this context, the current investigation focusses on the evolution of bifunctional CuZnAl (CZA)/ZSM-5 catalysts under the reaction conditions. One aims at assessing the microstructural changes within the catalyst with emphasis on the structure, morphology, chemistry of three dimensional distribution of the active phase on the support.

2. RESULTS

2.1 Experimental methodology

The mixed CZA catalyst with ZSM-5(13) zeolite was prepared by kneading of the mixture of powders in an agate mortar at a mass ratio of 5:3 (w/w) to form homogeneous hybrid catalyst, followed by pressuring the mixture into tablets and crushing them to 90–150 mesh size particles before the reaction. The DME synthesis reaction was carried out in a fixed-bed stainless-steel tubular reactor operating at 20 bar. To identify the effect of water on copper sintering, we conducted a specific experiment. In this experiment, water was added to the catalyst in a flow of hydrogen in the absence of carbon monoxide. The microstructural analyses have been carried out in a Jeol2100F TEM equipped with e C_s probe corrector under Scanning TEM (STEM) mode, an EDS detector and an EEL spectrometer. The approach used in the present study combines the electron tomography and Z contrast probed by the HAADF-STEM mode with the chemical and spatial selectivity of the STEM-EDS methodology. The samples were dispersed in ethanol and then deposited on carbon film supported by Ti or Mo grids. Three different specimens have been characterized: the fresh and the spent catalysts and most original, the specimen submitted to water vapors treatment. The tomography images were roughly aligned by cross-correlation and the final alignment has been achieved by using Au fiducial markers deposited on the membrane prior to specimen preparation. For the reconstructions, a 10 iteration ART procedure has been applied under ImageJ software, which has been employed also for the volume analyses.

2.2 Evolution of the catalyst morphology and the active phase distribution

After catalysts synthesis (the “fresh” catalyst) the Cu active phase locates preferentially on the ZnO and Al₂O₃ grains, as nanoparticles (NPs) with mean size of 10-20 nm and/or decorating the rims of the ZSM-5 grains and inner pores. The system high catalytic activity is correlated with the presence of NPs as well to the local Cu disposal as thin film on the surface of the ZSM-5. After reaction, the Cu remains located preferentially on the small CZA grains and on the ZSM edges, with an augmentation of the size of the active phase. The loss of contrast sharpness in the HAADF images is however noticeable. This is due either to the oxidation process occurring in the presence of CO, to the occurrence of a “coke” during reaction or both. Moreover, the catalytic activity of this bifunctional system decreases significantly. To get a deeper understanding on the mechanisms responsible for the catalysts deactivation, a water treatment has been performed, by employing similar amounts as the ones produced under reaction. Whilst the conversion of CO decreases rapidly from 60 to 10% after 24 h, the distribution of the Cu active phase surprisingly appears to be more homogenous on the CZA and ZSM-5 than

prior reaction. Since the 2D image alone cannot answer the question of active phase distribution in porous matrices as the ZSM-5, the approach advanced here implies the addition of electron tomography to the chemical contrast developed in STEM HAADF.

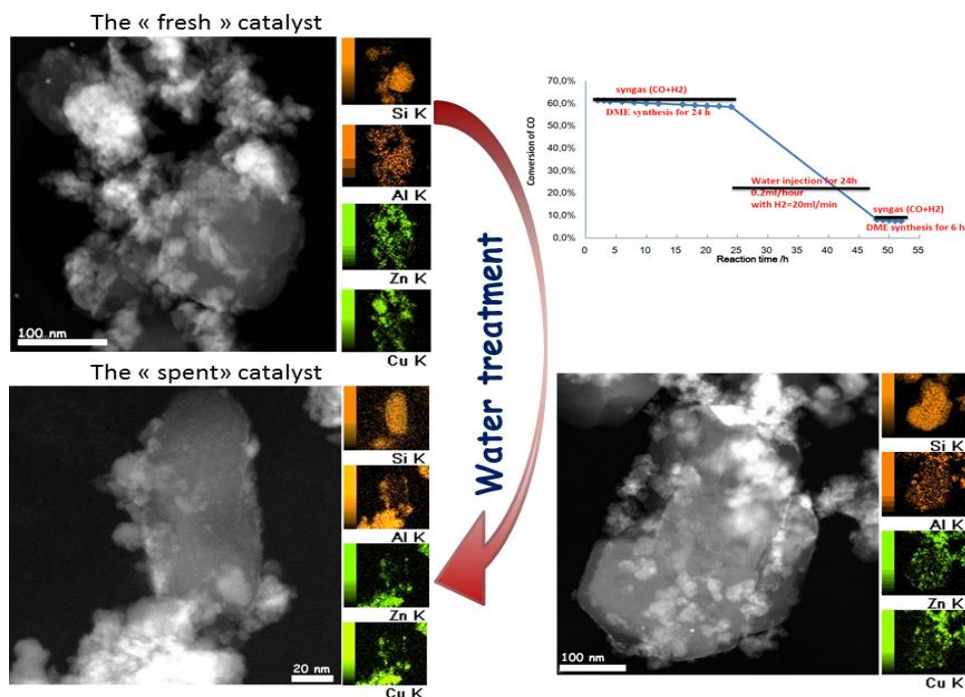


Figure 1. EDS STEM istudy of the morphology changes induced during the DME synthesis reaction (left). The effect of water treatment on the CO conversion rate and the catalyst 2D morphology (right)

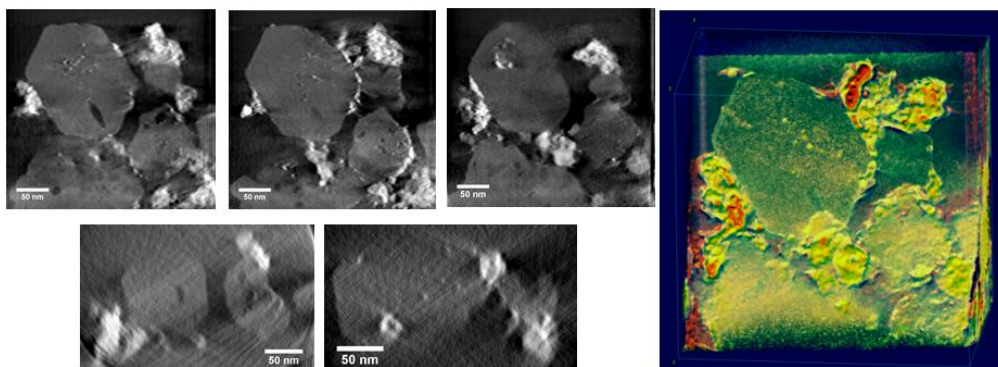


Figure 2. xy and xz sections (upper and lower row, respectively) redrawn from the reconstructed volume of CZA ZSM-5 specimen submitted to water treatment

Under the water vapors atmosphere, the active phase migrates and blocks the ZSM-5 pores, leading in this way to the strong diminishing of the system catalytic activity. Cu sintering in the presence of water is most probably accelerated as well by hydroxyl groups from the zeolite outer surface.

3. CONCLUSION

The microstructural evolution of bifunctional CZA ZSM-5 catalysts used for direct synthesis of DME has been carried out by using advanced systematical 2D and 3D STEM-based studies. This approach allowed one to assess for the microstructural changes induced by specific treatments and to corroborate them with the system catalytic response.

REFERENCES

- [1] Ordomy V.V., Cai M., Sushkevitch V., Moldovan S., Ersen O., Iancelot C., Valtchev V., Khodakov A.Y., Applied catalysis A, **486**, 266-275 (2014)