Supporting Information for ‘Synthesis of Cu-infiltrated Zr-doped SBA-15 catalyst for CO_2 hydrogenation into methanol and dimethyl ether’

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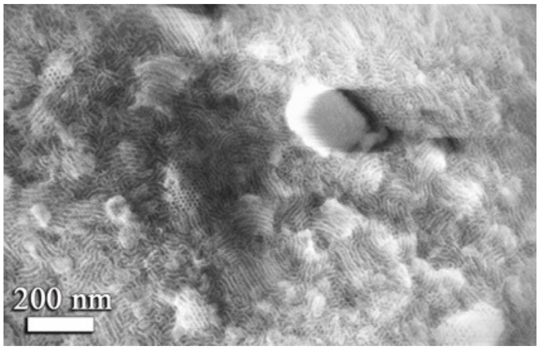

Figure S1. [Z]-Cl sample spherical particle at high resolution

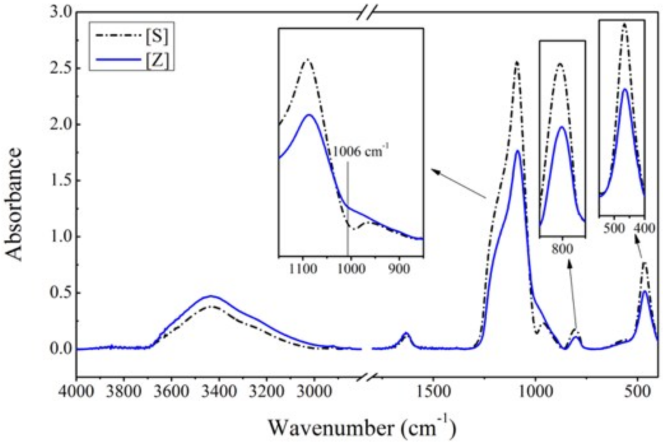

Figure S2. Transmission FTIR spectra of [S] and [Z].

The samples that are produced with various static times, hydrothermal treatment temperatures and times were obtained as rod shaped particle morphology with similar sizes. The flakes that are visible in the micrograph of St1 indicate incomplete particle evolution to its final morphology which is reached at 5 hours.

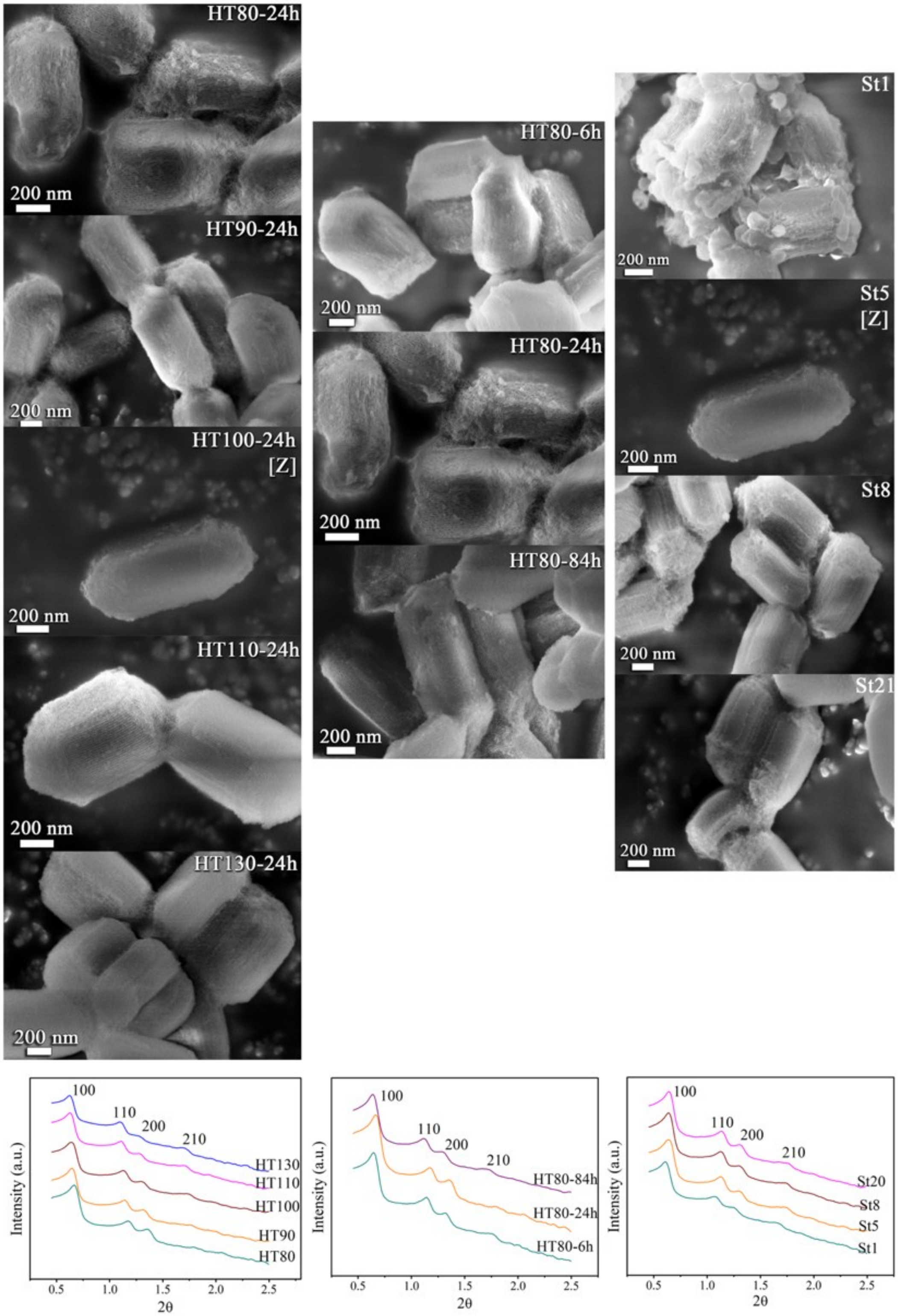

Figure S3. SEM micrographs of materials produced with different hydrothermal treatment temperatures (first column), times (second column), and static times (third column) and their corresponding small angle x-ray diffractograms.

The Cu nanoparticles grown on the mesoporous support have been obtained in different sizes. In order to estimate the Cu nanoparticle sizes, they were divided in 2 groups: relatively small nanoparticles located in the pores of the mesoporous support and bigger ones that are located on the outer surface of the submicron particles of the support. Thus, one of the strongest peaks of CuO nanoparticles (at 2θ=35.5 °) was fitted to two peaks. Full-width half-maximum of these fitted peaks were used to calculate two different CuO nanoparticle sizes.

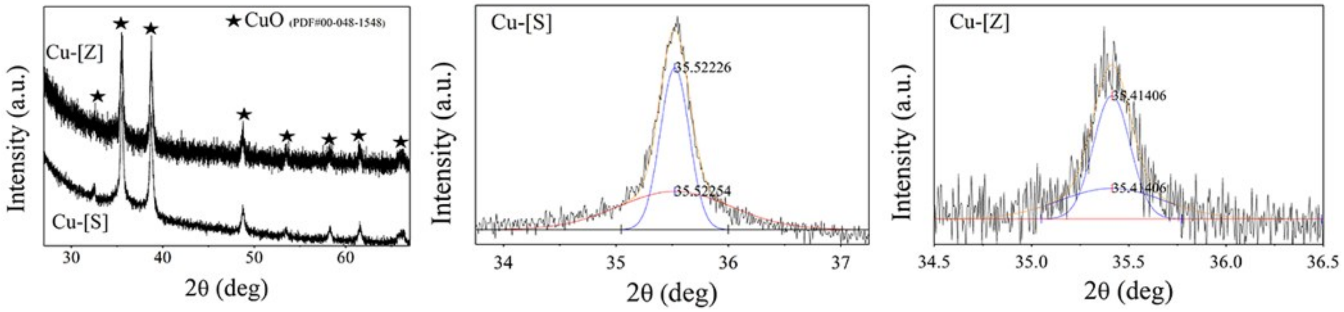

Figure S4. X-ray diffractograms and peak fitting of a CuO peak for Cu-[Z] and Cu-[S].

Cu infiltration involved functionalization of [S] and [Z] prior to Cu addition. The outer surface of the particles (before calcination) were functionalized with TMCS (trimethylchlorosilane) and this way methyl groups are attached on the external surface of the particle. Following s calcination step at 300 °C for 5 hours, the internal surface was functionalized with APTMS (3-aminopropyl trimethoxysilane) and this way amine groups are attached on the pore surfaces. The functionalization caused a shift in the mesopore size change as well as a distortion in the isotherms (see Figure S5).

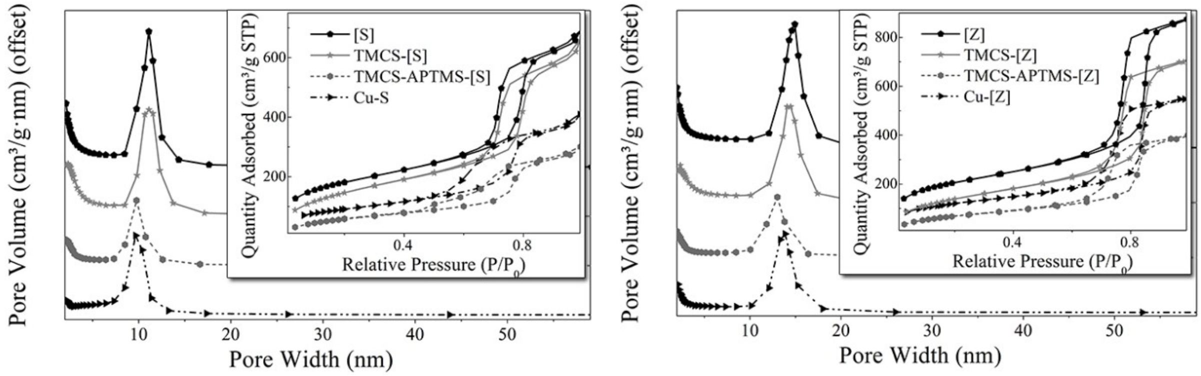

Figure S5. Isotherms and pore size distribution evolution of the particles during different steps of the Cu infiltration.

TMCS functionalization decreased pore volume while pore size remained the same. This is due to lower calcination temperature which caused most of the P123 to decompose except a small amount located possibly in the micropores. On the other hand, the mesopore size is independent of the TMCS functionalization indicating that 300 °C is high enough to empty the mesopores which is necessary for Cu nanoparticle growth. Both APTMS functionalized and Cu loaded samples have distorted desorption curve indicating that amine groups and Cu nanoparticles are present in the pores. This points out efficient use of the high surface area for growing Cu nanoparticle.

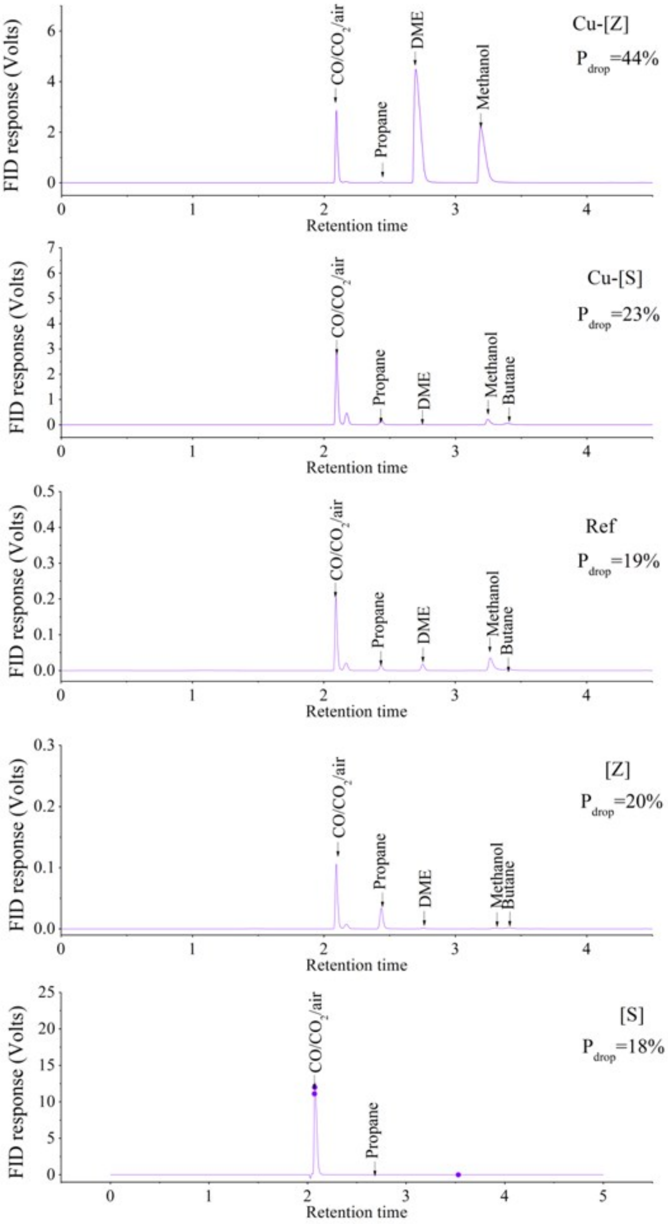

Figure S6. FID signals obtained from the final gas mixtures of the reactions catalyzed with Cu-[Z], Cu-[S], Ref, [Z] and [S].

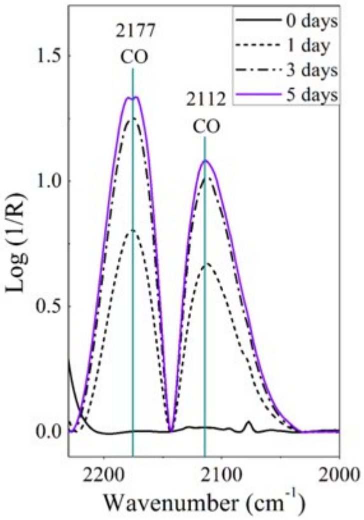

Figure S7. DRIFT spectra of CO peaks at time points: 0, 1 day, 3 days, and 5 days.