Electronic Supplementary Material

Direct synthesis of dimethyl ether from CO_2 hydrogenation over Cu–ZnO–ZrO_2/SO_4^{2-}–ZrO_2 hybrid catalysts: Effects of sulfur to zirconia ratios

Thongthai Witoon [a, b, c, d*], *Tinnavat Permsirivanich* [a], *Nawapon Kanjanasoontorn* [a], *Chalairat Akkaraphataworn* [a], *Anusorn Seubsai* [a], *Kajornsak Faungnawakij* [e], *Chompunuch Warakulwit* [b,c], *Metta Chareonpanich* [a,b,c,d*] *and Jumras Limtrakul* [b,c,d]

[a] Center of Excellence on Petrochemical and Materials Technology, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

[b] Center for Advanced Studies in Nanotechnology and Its Applications in Chemical Food and Agricultural Industries, Kasetsart University, Bangkok 10900, Thailand

[c] NANOTEC-KU-Center of Excellence on Nanoscale Materials Design for Green Nanotechnology, Kasetsart University, Bangkok 10900, Thailand

[d] PTT Group Frontier Research Center, PTT Public Company Limited, 555 Vibhavadi Rangsit Road, Chatuchak, Bangkok, 10900, Thailand

[e] Nanomaterials for Energy and Catalysis Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSDTA), Klong Luang, Pathumthani 12120, Thailand

*Corresponding author: Tel.: +66 2579 2083; Fax: +66 2561 4621
E-mail address: fengttwi@ku.ac.th (Thongthai Witoon)
fengmtc@ku.ac.th (Metta Chareonpanich)

Catalyst characterization

The apparent morphology of the sulfated zirconia catalysts after calcination at 550 ^oC was examined by means of SEM; the result is shown in Fig. 1S. In the absence of sulfur (ZrO_2), a rod-like structure with a smooth surface was formed. Incorporating ammonium sulfate into the ZrO_2 cluster leads to a significant change in the shape and surface of the catalysts. At low sulfur content (5S-ZrO_2, 10S-ZrO_2 and 15S-ZrO_2), the catalysts appear to possess a rough surface with

a lot of voids. When sulfur content is increased from 15 to 30 wt%, the surfaces of the catalysts become rougher and the void sizes were significantly expanded. This indicates that the presence of ammonium sulfate acts as a space-filling agent, which possibly leaves an empty space during the calcination process. Note that the increase in the void size with increasing sulfur content is consistent with the results of the pore size distribution previously mentioned in Fig. 1.

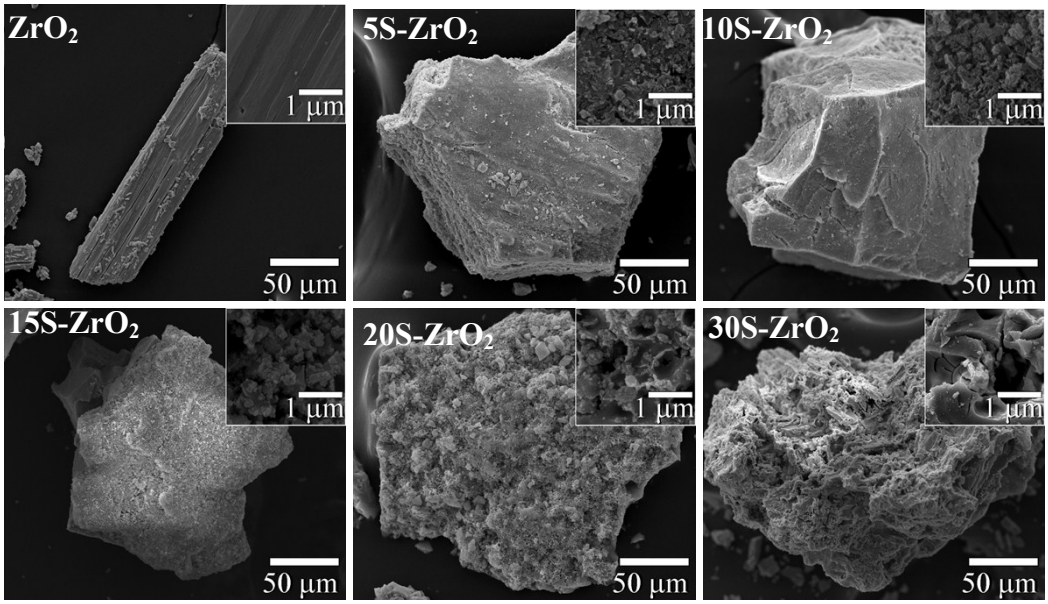

Figure 1S SEM images of sulfated zirconia catalysts calcined at 550 ^{o}C.

The XRD patterns of the calcined sulfated zirconia catalysts prepared at different sulfur loading contents are presented in Figure 2S. The XRD pattern of pure zirconia appears the major peaks at 2θ angles of 24.1, 28.2, 30.1, 31.4, 34.1, 34.3, 49.3, 50.1, 50.2 and 60.0^{o} corresponding to the presence of a mixture of monoclinic and tetragonal phases. The XRD pattern of the sulfated zirconia catalysts shows 2θ angles identical to those of the pure zirconia. However, the peak intensities of the sulfate modified zirconia catalysts gradually decrease with increasing sulfur content, implying that the ZrO_2 becomes less crystalline. This suggests that the

presence of the sulfate species acts as a building block unit which prevents the agglomeration of the ZrO_2 nanoparticles and results in the suppression of phase transformation.

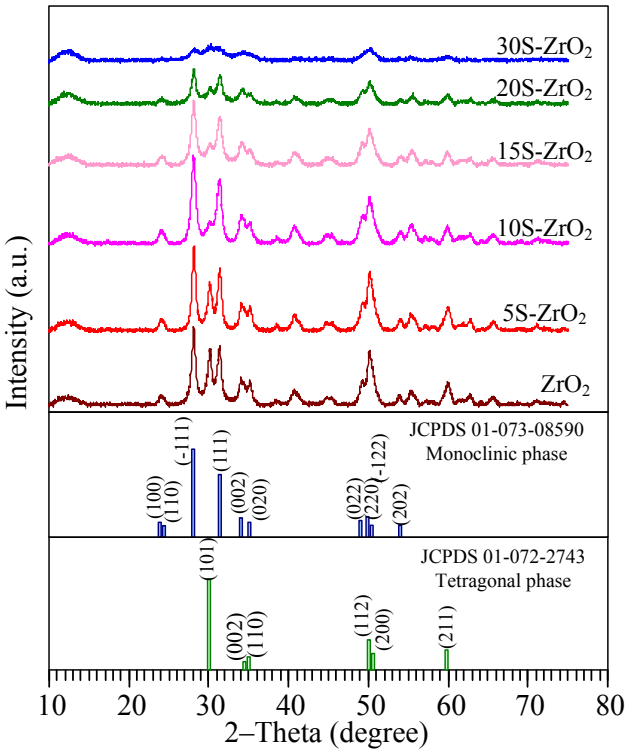

Figure 2S XRD patterns of the sulfated zirconia catalysts calcined at 550 °C.