From CO_2 to dimethyl ether: mesostructured acidic oxides for methanol dehydration to design bifunctional catalysts

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CO_2 is widely recognised as the main cause of greenhouse effect, causing global warming and climate change. With the aim to reduce CO_2 emissions, during the last decades, several strategies have been developed for the capture, utilization and storage of carbon dioxide (CCUS). This work focuses on the development of bifunctional catalysts for the conversion of CO_2 into dimethyl ether (DME), a fuel with no collateral emissions other than CO_2 and H_2O, a high cetane number and chemical-physical properties similar to LPG. DME is obtained from the reaction of CO_2 with H_2 through two subsequent reactions. The first one is the CO_2 reduction with H_2 to obtain methanol; this reaction is promoted by Cu-based catalysts like $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$. The second one is the dehydration of methanol to DME, catalysed by solid acidic catalysts, such as zeolites and γ-Al_2O_3 [1,2]. The two reactions are reported below:

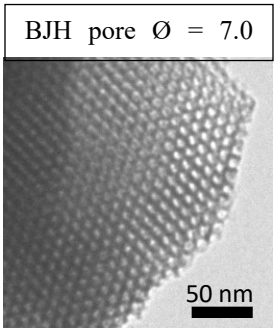
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^0_{298K} = -49.5\ kJ/mol$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H^0_{298K} = -23.4\ kJ/mol$$

The global reaction is, thus:

$$2CO_2 + 6H_2 \leftrightarrow CH_3OCH_3 + 3H_2O \qquad \Delta H^0_{298K} = -123\ kJ/mol$$

In this work three different types of mesostructured acidic catalysts were synthesized: Al-SiO_2 (Al-SBA-15, Al-MCM-41), Zr-TiO_2 and γ-Al_2O_3.These materials were tested for methanol dehydration and used as supports for the Cu-based redox phase, to obtain composite materials to be used as bifunctional catalysts. Mesostructured matrix should limit the growth of redox phase nanoparticles inside the mesopores and assure a high dispersion due to the high surface area, leading to a high contact area between the two phases and, thus, granting in principle superior catalytic performances.



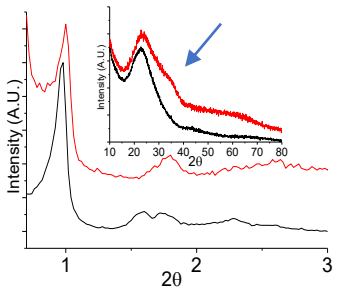
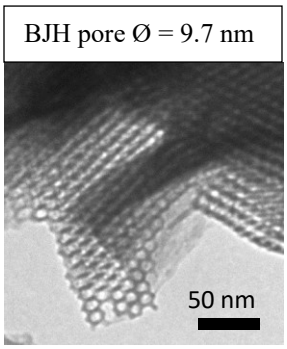


Figure 1. TEM and XRD of Al-SBA-15 (black) and composite (red)



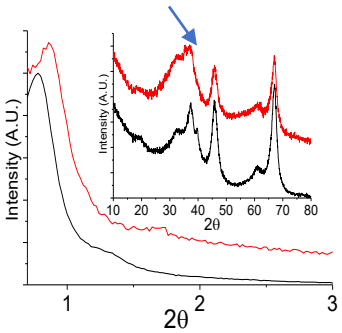


Figure 2. TEM and XRD of γ-Al_2O_3 (black) and composite (red)

All mesostructured systems were synthesized via the Sol-Gel method, either through an Evaporation-Induced Self-Assembly (EISA) or a solvothermal approach, and characterized by XRD, TEM and N_2 physisorption. Acidic sites characterization was performed by calorimetry and FTIR spectroscopy using pyridine as a probe molecule. The catalysts were eventually physically mixed with a $Cu/ZnO/Al_2O_3$-based commercial redox catalyst and tested in a bench-scale plant with a fixed bed reactor for CO_2 conversion to DME. Mesostructured supports were used to disperse the $CuO/ZnO/ZrO_2$-based redox phase by a wet impregnation method combined with a self-combustion process or by a two-solvents impregnation strategy. The obtained bifunctional catalysts were characterized by PXRD, N_2 physisorption, TEM and HRTEM in order to determine the most promising synthetic conditions in terms of dispersion and nanosize of the active phase and textural properties of the corresponding composites.

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