Design of bifunctional catalysts from mesostructured acidic oxides for CO_2 conversion to dimethyl ether

Fausto Secci[a], Claudio Cara[a], Elisabetta Rombi[a], Marco Sanna Angotzi[a], Sarah Lai[b], Kai Skrodczky[c], Nicola Pinna[c], Mauro Mureddu[b], Carla Cannas[a]

[a] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.P. Monserrato Sestu km 0.700, 09042 Monserrato (CA), Italy

[b] Sotacarbo SpA, SS126, 09013 Carbonia (CI), Italy

[C] Department of Chemistry, Humboldt University, Berlin, Germany

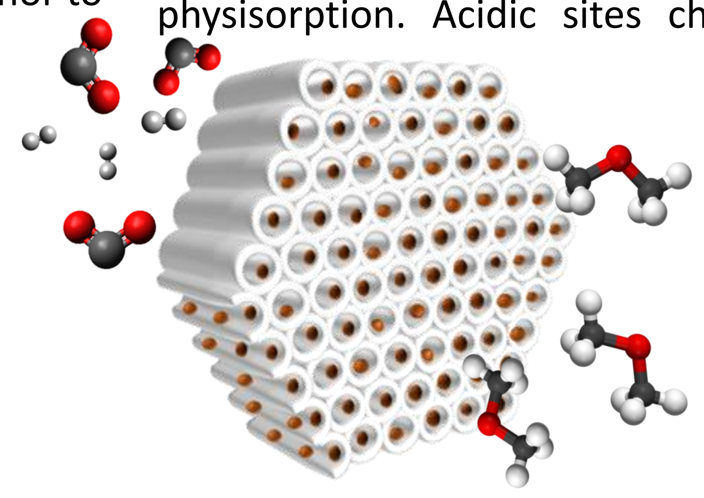
Introduction

CO_2 is widely recognized as the main cause of global warming and climate change. With the aim to reduce CO_2 emissions, 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]. 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, 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. All mesostructured systems were synthesized via the Sol-Gel method 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 commercial redox catalyst and tested in a bench-scale plant. 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. The obtained bifunctional catalysts were characterized 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.

[1] A. Alvarez, A. Bansode, A.Urakawa et al. Chem. Rev., 2017, 117, 9804-9838.

Mesostructured acidic catalyst

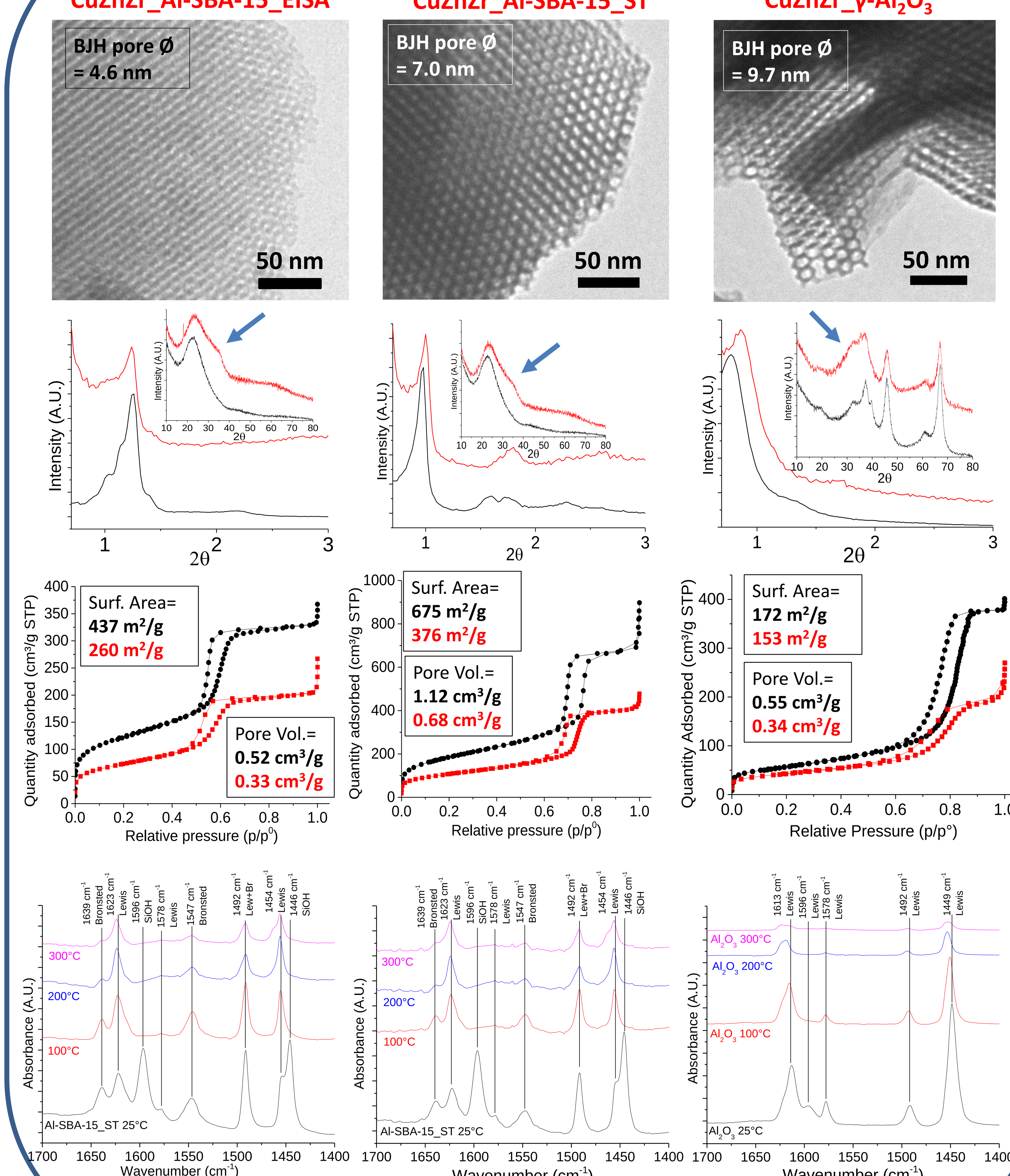
Functionalization →



Mesostructured bifunctional catalyst

Characterization

Al-SBA-15_EISA	Al-SBA-15_ST	γ-Al_2O_3
CuZnZr_Al-SBA-15_EISA	CuZnZr_Al-SBA-15_ST	CuZnZr_γ-Al_2O_3



Synthetic route

Evaporation-Induced Self-Assembly Sol-Gel Al-SBA-15_ST, Zr-TiO_2, γ-Al_2O_3

Block copolymers and precursors in ethanol under acidic conditions
↓ Stirring
Evaporation under controlled humidity and temperature conditions
↓ Aging
Thermal treatment

Solvothermal Sol-Gel Al-SBA-15_EISA

Block copolymers and precursors in water under acidic conditions
↓ Stirring
Solvothermal treatment into an oven
↓ Washing
Thermal treatment

Functionalization

Wet impregnation modified with a self-combustion process

Mesostructured support put into a beaker
↓ Stirring
Addition of an aqueous solution of Cu, Zn and Zr nitrates and glycine
↓ Evaporation of water
Thermal treatment

Catalytic tests

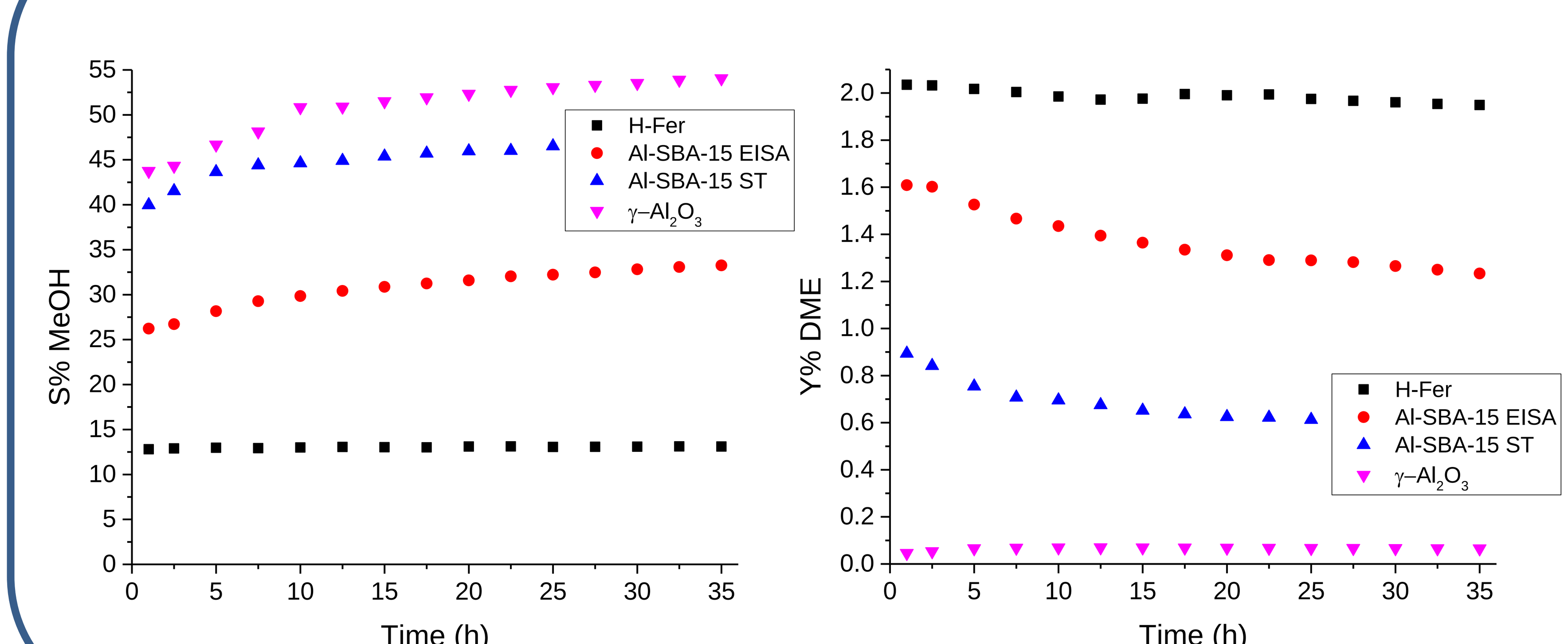
All methanol dehydration acidic catalysts were tested in **XtL Plant** at **Sotacarbo SpA**

Reactor technical specifications:

- **Type:** fixed bed reactor
- **Working range:** up to 700 °C at 10 MPa
- **Analysis system:** GC online equipped with TCD and FID detector.

Methanol dehydration acidic catalysts were tested in physical mixture with CZA ($Cu/ZnO/Al_2O_3$-based commercial redox catalyst).

Catalytic performance



Conclusions and future perspectives

- EISA and Sol-Gel methods allowed to obtain ordered mesoporous metal oxides.
- These materials have been characterized to gather information about mesostructure (LA-XRD, TEM), morphology (TEM), crystallinity (WA-XRD), textural properties (N_2 physisorption) and acidic sites (FTIR, calorimetry).
- Catalytic tests showed steady activity towards methanol dehydration for all tested mesostructured oxides; the best mesostructured catalyst, in terms of methanol dehydration, is Al-SBA-15 obtained through EISA.
- All mesostructured oxides have been functionalized with a redox phase ($Cu/ZnO/ZrO_2$) via a wet impregnation method modified with a self-combustion process, to obtain bifunctional catalysts.
- The ordered mesoporous structure should allow to obtain a uniform dispersion of the redox catalyst with a high contact area and between the two phases. Furthermore, the ideal pore size will limit the growth of redox NPs avoiding sintering phenomena.
- All bifunctional catalysts well be tested for DME production from CO_2 and H_2 and compared with commercial catalysts.