

Ordered Mesoporous SBA-15 Silica as Support for MeO_x (Me=Zn, Fe) Nanophases Fabricated by “Two-Solvents” Strategy



Nanophases Fabricated by “Two-Solvents” Strategy



Mauro Mureddu^{1,2}, C. Cannas^{1,2}, E. Rombi¹, I. Ferino¹, M.G. Cutrufello¹, A. Ardu¹, G. Piccaluga¹, A. Musinu¹

¹ Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, Cittadella Universitaria, 09042, Monserrato, (CA) Italy

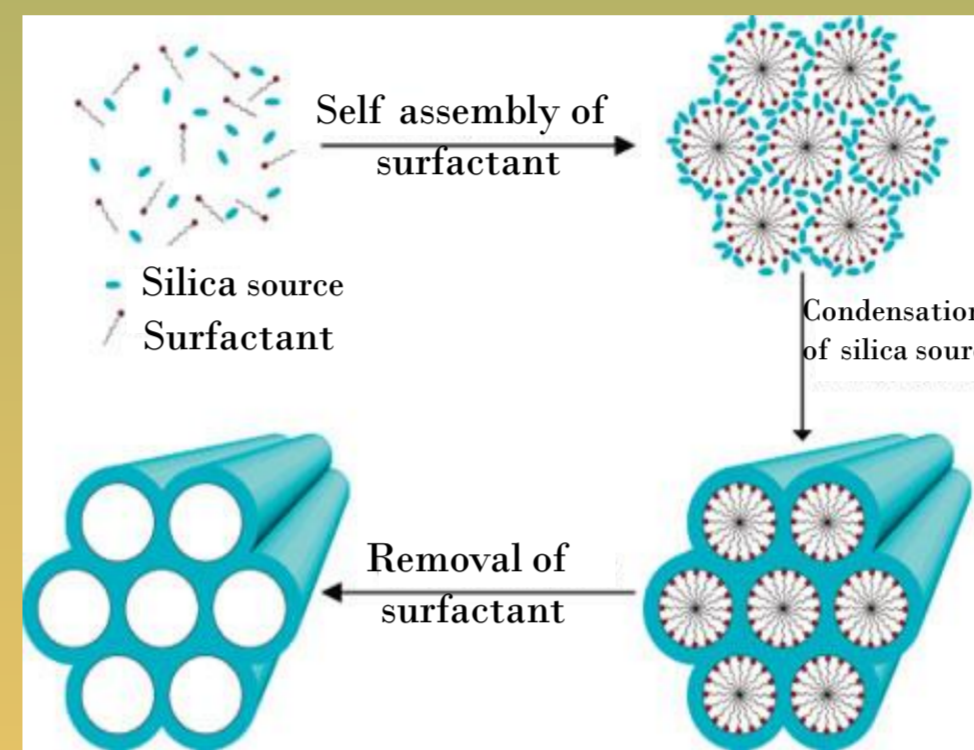
² Consorzio AUSI, Consorzio per la promozione delle Attività Universitarie del Sulcis-Iglesiente, Palazzo Bellavista Monteponi, 09016, Iglesias (CI) Italy

contact: mauromureddu@unica.it

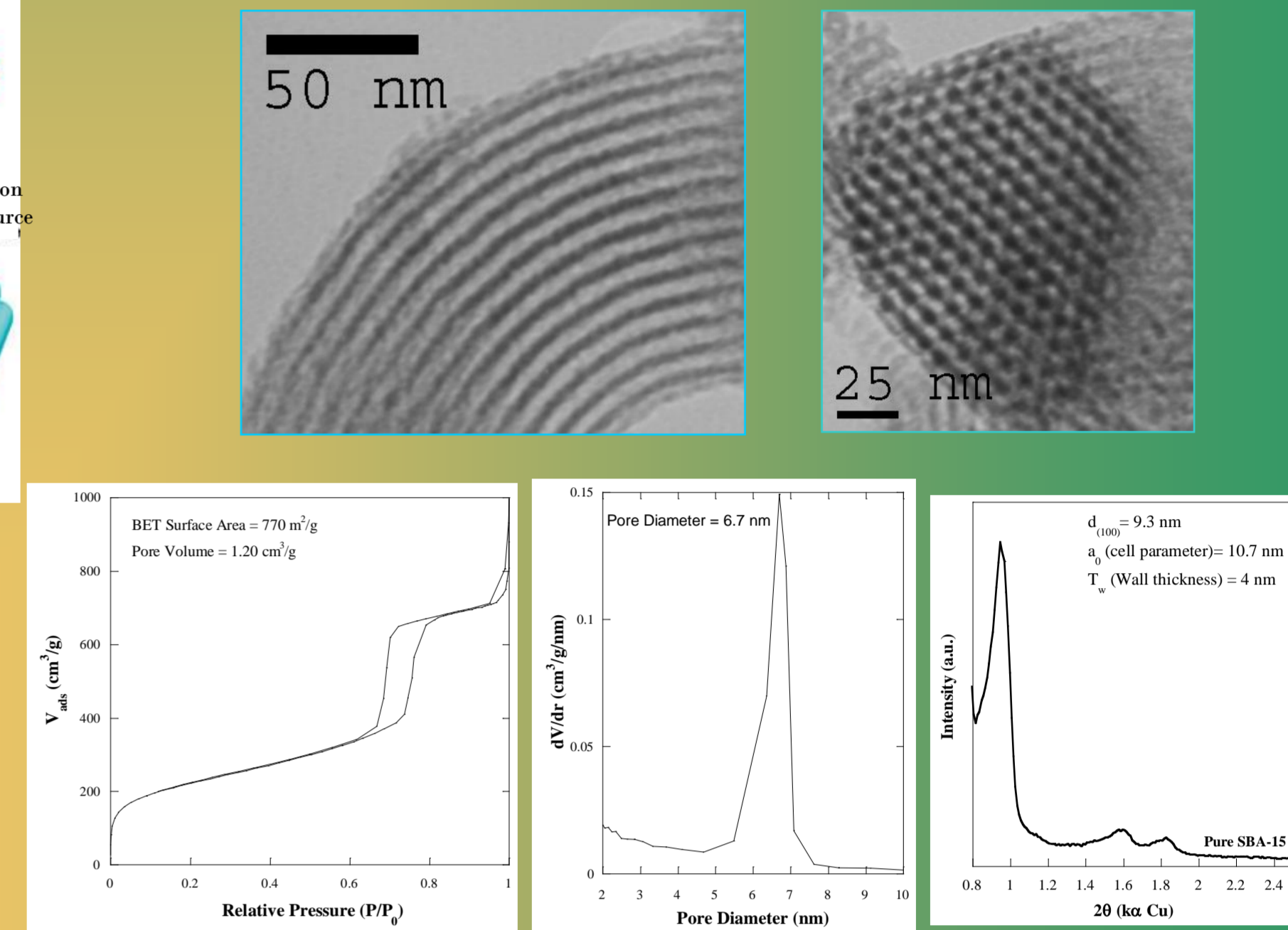
Introduction

Ordered mesoporous silica materials are one of the most important scaffolds for constructing advanced nanocomposites at the nanometer scale. The confined growth of solids inside the mesopores of silica matrices within the so-called “host-guest chemistry” framework has gained a lot of attention in the past few decades. Among the silica compounds available as hosts, SBA-15 can be regarded as the simplest one due to its regular 2D porous network constructed by hexagonally arranged straight mesopores connected by bridging micropores. Its characteristics, such as tunable pore size, narrow pore size distribution, large specific area (up to 1000 m²/g), thermal and mechanical stability, fairly good chemical inertness, make this material very attractive for many applications, such as catalysis, biosensing, environmental studies and energy storage. In this work, we report the SBA-15 silica used as support to stabilize metal oxide nanophases within its mesochannels, as a class of nanosorbents for the chemical H₂S removal. In this framework, Hydrogen sulphide is considered as one of the most noxious industrial gases for the atmosphere, a well-known poison for metallic catalysts, and its concentration in feedstocks should be decreased to 10-100 ppb before their use. To accomplish this task, Zinc oxide and Iron oxide based materials have been successfully employed for decades in different domains of the chemical industry. The pure metal oxides used as sorbents, however, suffer from evaporation, loss in the surface area and porosity due to sintering and mechanical disintegration that affect their performance and lifetime adversely [1]. With the purpose of overcoming this problem and to improve their performance, metal oxides nanophases have been incorporated into the inert SBA-15 support. Such a structure provides an ideal reactor where the mesopores act as channels for the transport of reactant [2]. Under such conditions the nanostructure materials are stable, being the mesostructure retained up to high temperature, and they exhibit a higher reactivity toward H₂S in comparison with classical sorbents consisting of micrometer-sized particles.

SBA-15 Mesostructured Silica



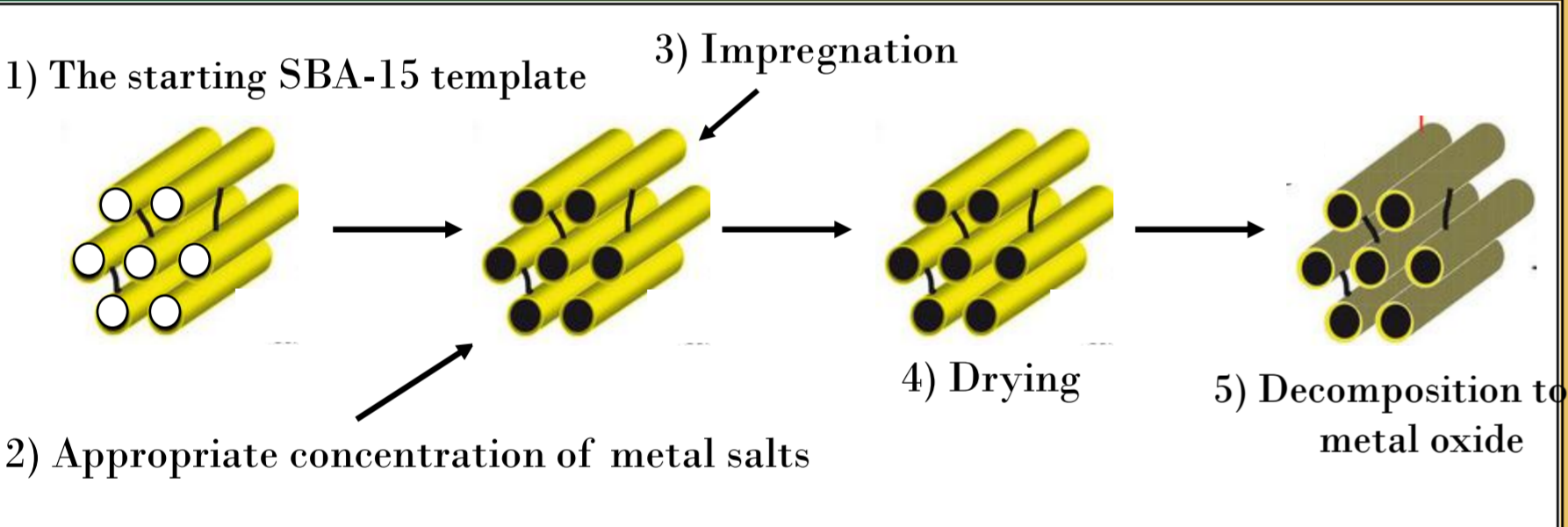
- High-surface area (up to 1000 m²/g)
- Narrow distribution of mesopores
- Hexagonally arranged mesopores
- High percentage of hydroxyl groups on channels' walls
- Great chemical, thermal and mechanic stability



Impregnation Route

- Simplicity
- High-surface area
- High dispersion at different loadings (wt%)

The pore filling process aims at filling the mesopore channels with the precursor solution

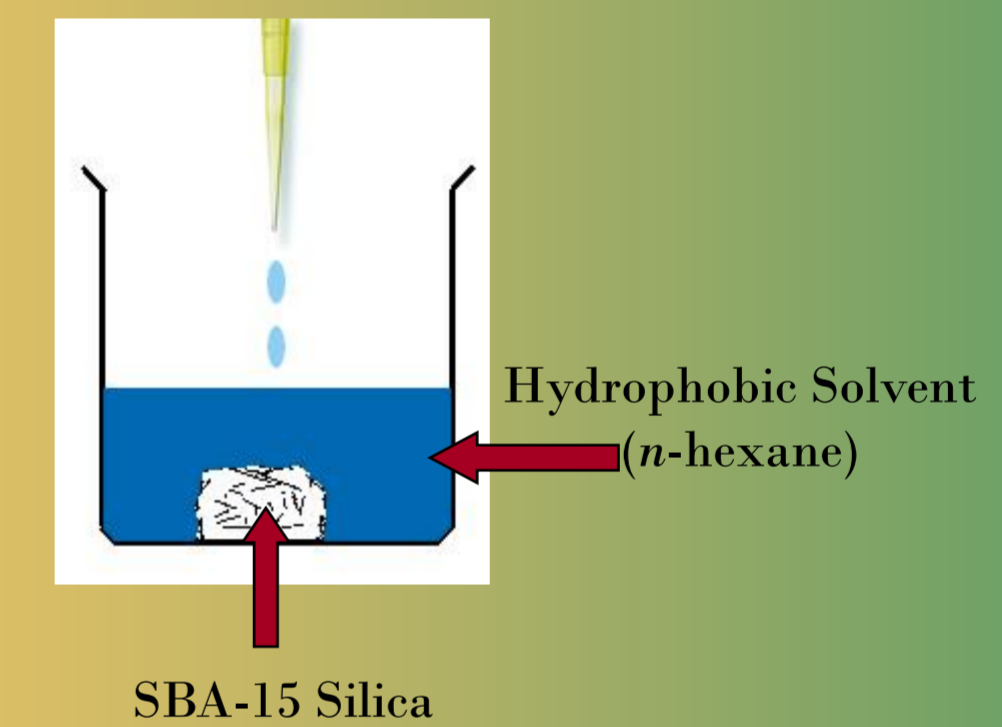


Nanocomposites Fabrication

Two-Solvents Impregnation Technique

..is based on the suspension of dried silica inside a first hydrophobic solvent (n-hexane) before the addition of a volume of aqueous solution containing the metal oxide precursor and set equal to the porous volume of the support (determined by N₂ physisorption)

Metal Precursor Aqueous Solution (Zinc or Iron Nitrate)

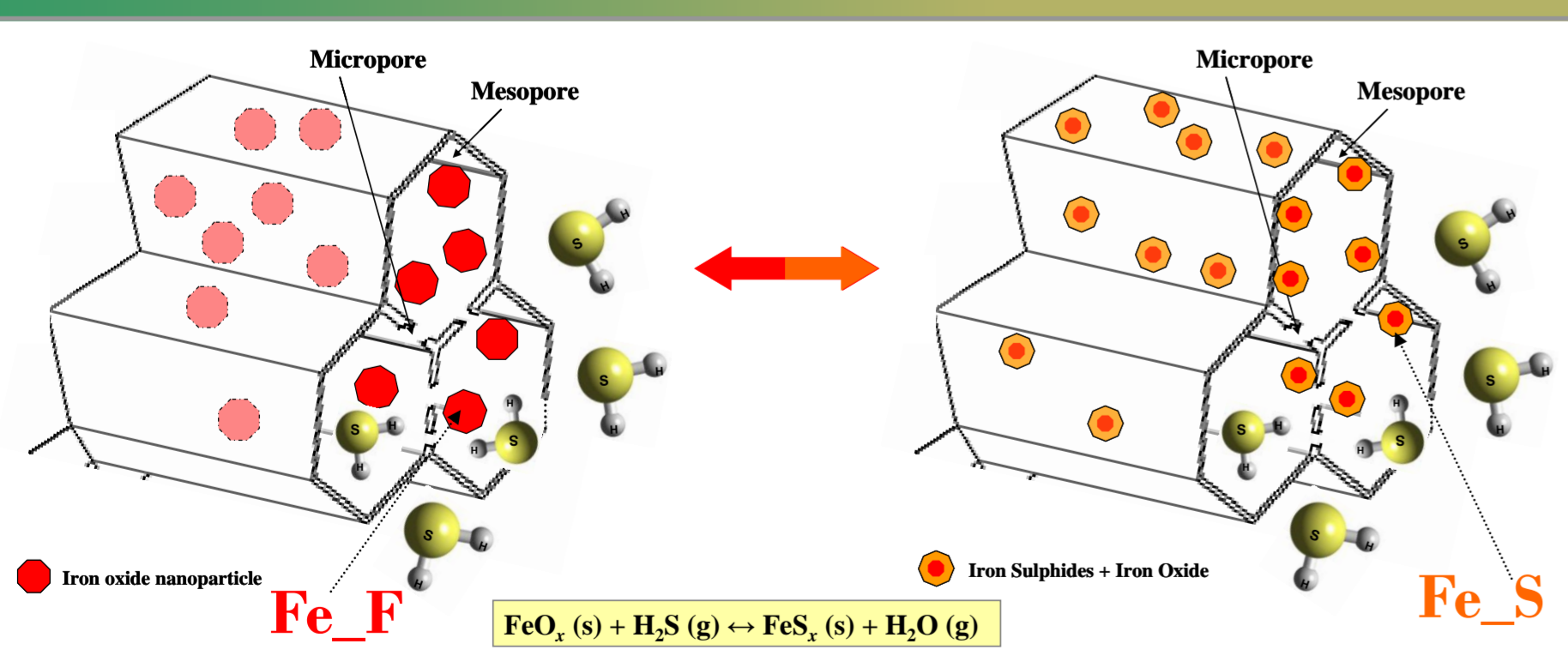
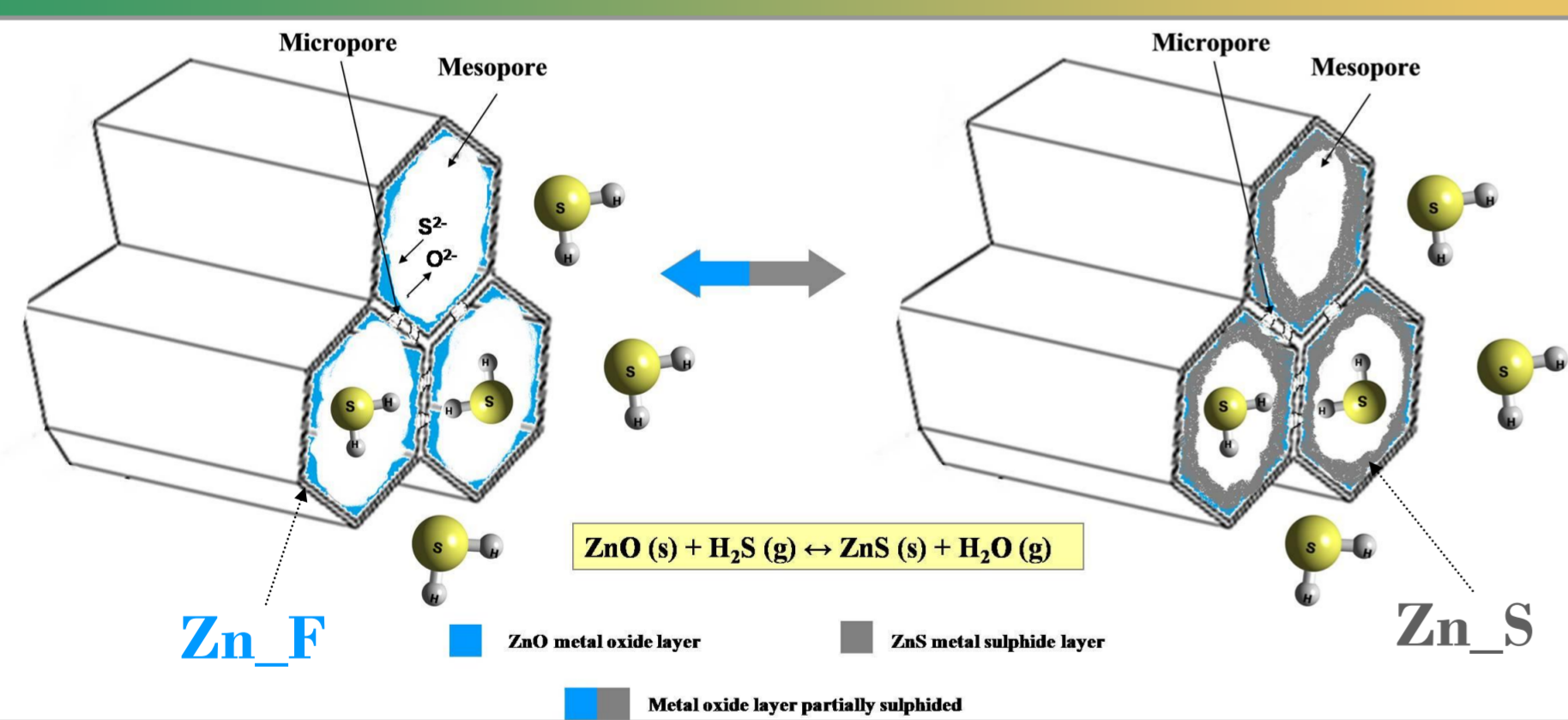
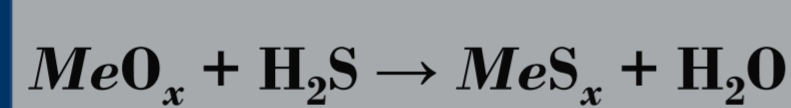


Vigorous stirring + Drying step + Calcination in air at 500 °C



Zinc & Iron oxide@SBA-15 Results

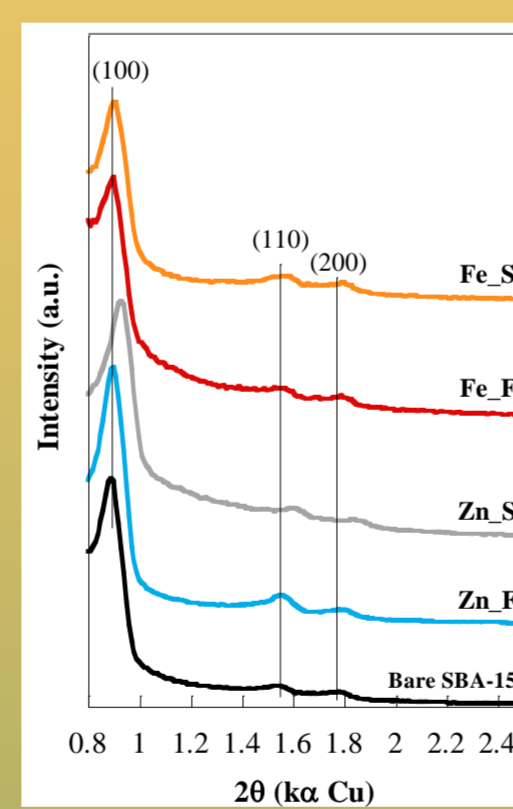
Desulphurization Activity



Sample	Run number ^a	Breakthrough time (s)	Retention capacity (mg/g _{active phase})	Retention capacity (mg/g _{Sorbent})
Katalco301	1	103	6	6
	2	26	2	2
	3	26	2	2
Zn	1	180	53	10
	2	230	68	13
	3	310	92	18
Fe	1	1350	401	80
	2	670	199	40
	3	750	223	45

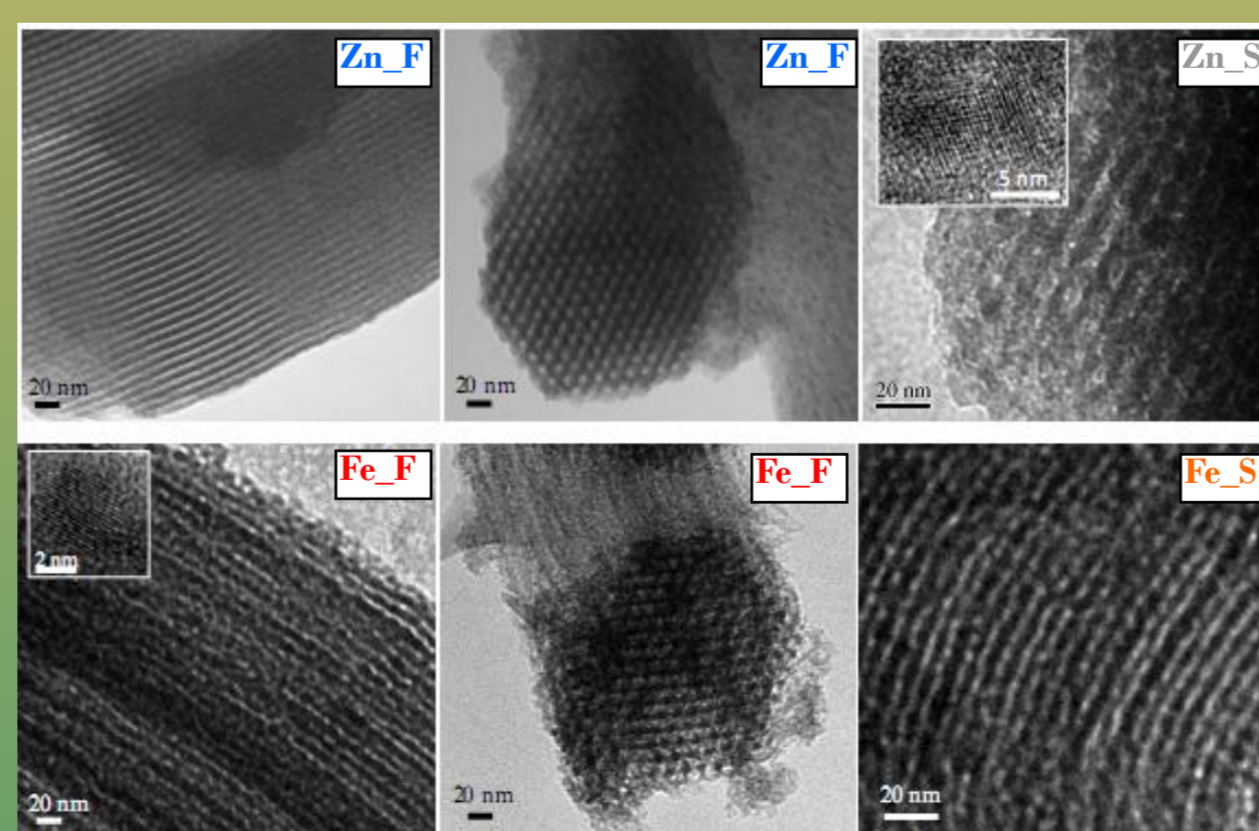
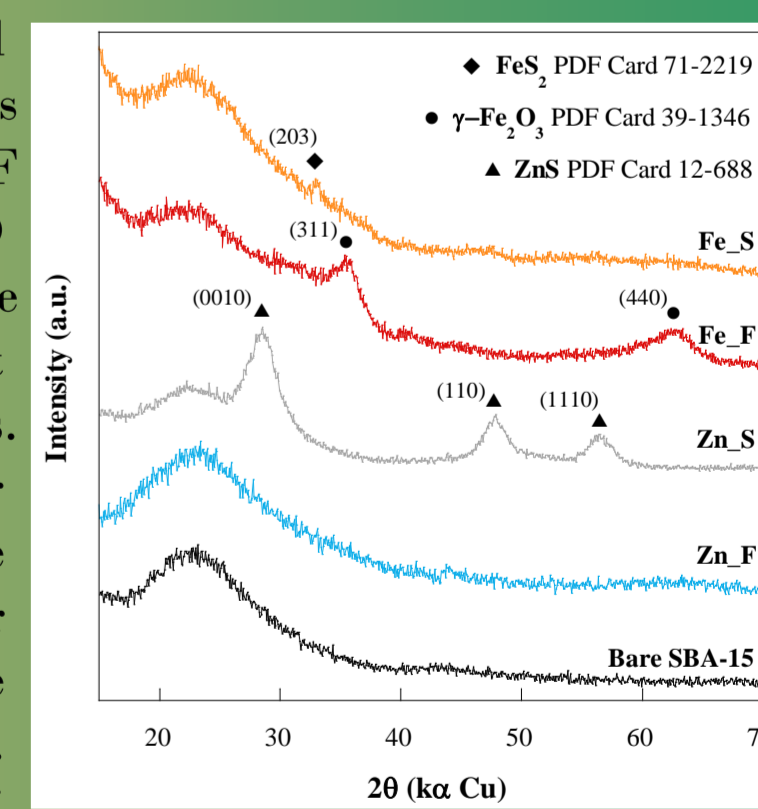
The highest retention capacity is obtained for the Fe_F sorbent, being more than seven-times higher than that of the Zn_F sorbent, and even much more higher than the corresponding value for the commercial ZnO sorbent. The by far superior performance of the SBA-15 supported sorbents with respect to that commercial sample can be reasonably ascribed to differences in the exposure of the active phase to the reactant H₂S.

Fresh and Sulphided Sorbents Characterization



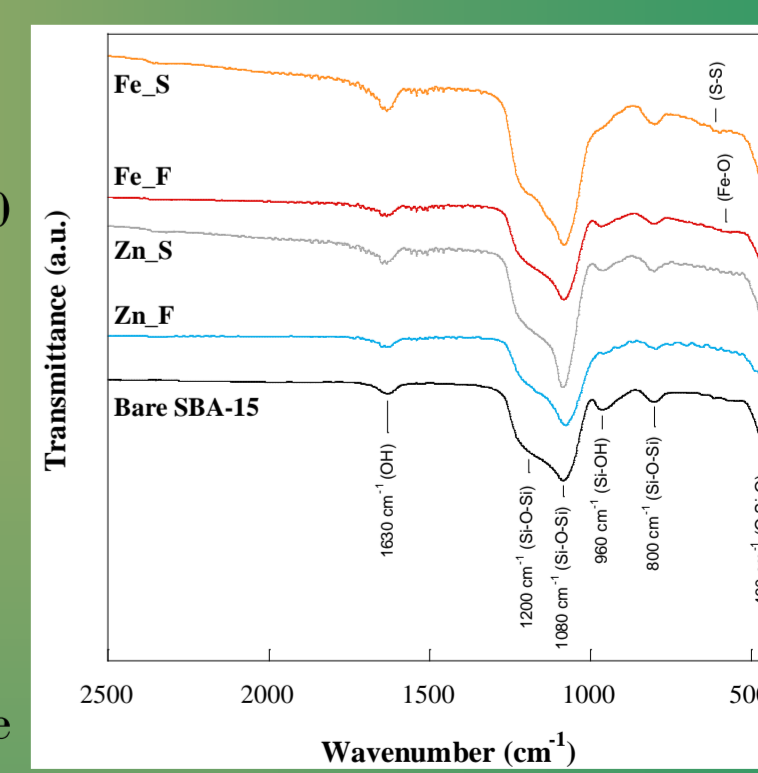
A slight shift of the reflections towards higher angles can be observed for both sorbents, suggesting a small contraction of the cell parameters.

The wide-angle diffraction pattern of all samples show the typical haloes of amorphous silica at 2θ = ca. 23°. In the pattern of Zn_F no diffraction peaks corresponding to ZnO phase are observable, indicating that the active phase is well dispersed into/over the support as an amorphous phase or as nanocrystals. The pattern of Fe_F exhibits two further broad peaks that can be attributed to the most intense reflections of maghemite. For Zn_S, clear and intense reflections are present, easily assigned to ZnS phase. A small peak is observed in the pattern of Fe_S, attributed to the most intense reflection (101) of the FeS₂ pyrite phase.



No isolated ZnO particles are visible onto the external surface or inside the pores of Zn_F. From the increase of the walls thickness, the formation of an amorphous and rather uniform thin layer of zinc oxide has occurred at the inner surface of the pore walls. The Fe_F images show that iron oxide is not uniformly dispersed; note the rough contours of the channels (some of which appear completely filled). In the Zn_S sorbent, the particles are mainly anchored at the channel walls, whose contours appear rather rough, with a rope-like profile. No significant differences between the fresh and sulphided sorbent are visible in the TEM micrographs for the Fe_S sample.

The spectrum of the Fe_F sorbent exhibits a small broad band due to Fe-O stretching at about 550 cm⁻¹; the Zn-O stretching at 460 cm⁻¹ is not visible in the Zn_F spectrum, due to the overlapping with the O-Si-O bending signal. Interestingly, the band at 960 cm⁻¹ is still clearly visible after the incorporation of the iron oxide phase, whereas it is absent in the case of Zn_F sorbent, which supports the occurrence of the interaction between the ZnO phase and the silica matrix.



The presence of FeS₂ phase, revealed by the XRD patterns and the pale brass-yellow color of Fe_S, can be responsible for the low-intensity band at 600 cm⁻¹

Acknowledgements

This work was financed by Consorzio AUSI (Consorzio per la promozione delle Attività Universitarie del Sulcis-Iglesiente).