Regenerable MeO/SBA-15 nanocomposites for mid-temperature H_2S removal from syngas coal gasification

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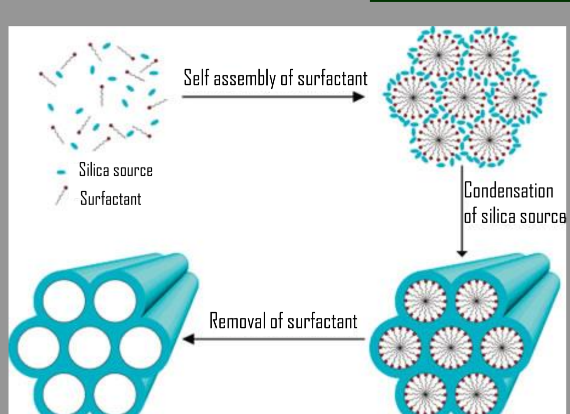
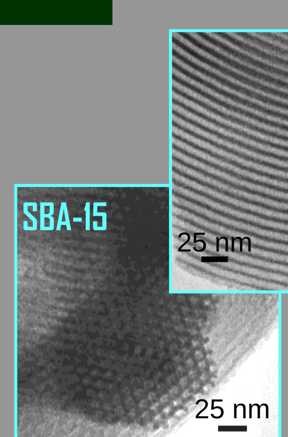
Introduction

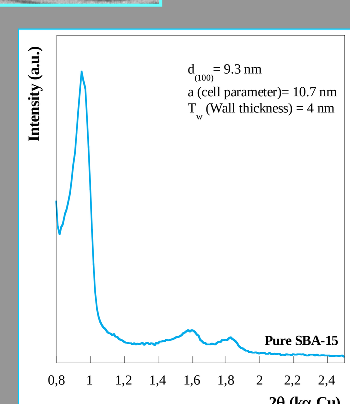
These days the possible depletion of earth's fossil fuel resources and the associated environmental problems have become international concerns in the field of energy. Therefore, the development of clean and efficient coal utilization technologies is very important for the world. Raw gas produced from the IGCC gasification, the most efficient and environmentally acceptable technology, contains a lot of pollutants, including Hydrogen Sulfide (H_2S), the main contaminant for air environment and for the damage to human health, water resource, catalyst poisoner and can cause pipeline corrosion thus limiting plant lifetime [1]. Zinc oxide is among the most favorable oxides to be used to remove H_2S in above technologies for his high reactivity, high equilibrium constant and ability of ZnS to be regenerated. Unfortunately, despite the favourable thermodynamics, if used as pure phase, the temperatures used during the sulphurization cycle and regeneration can cause the sintering of the particles and therefore the decrease of specific surface area and, consequently, of the performance. To overcome this drawback, *Me*O/SBA-15 composite sorbents (*Me*= Zn, Fe) with good performance for mid-temperature H_2S removal were synthesized in a wide range of the active phase loading.

Mesostructured SBA-15 silica is a high-surface area (up to 1000 m^2/g) material, with 6-7 nm-wide regular channels and thick (3-4 nm) pore walls. By the confinement of the active phase into the mesoporous channels of SBA-15, control of the particle size on a nanometric scale might be achieved. As a consequence, enhancement of the active phase reactivity might be expected. Remarkable sulphur retention capacity referred to the active phase was shown by the composites if compared with a commercial sorbent. At variance with the case of the commercial product, the sorption properties are enhanced after regeneration and maintained upon repeating the sorption/regeneration cycle [2]. Nanocasting route has been selected to produce all the composites. The overall results show: (i) the confinement of the active phase into the ordered channel system of mesostructured SBA-15 achieved by both Incipient Wetness and Two-Solvents impregnation strategies; (ii) the sorption behaviour not strictly dependent on the surface area and pore volume features of the composites, which are usually assumed as key parameters.

Host Material



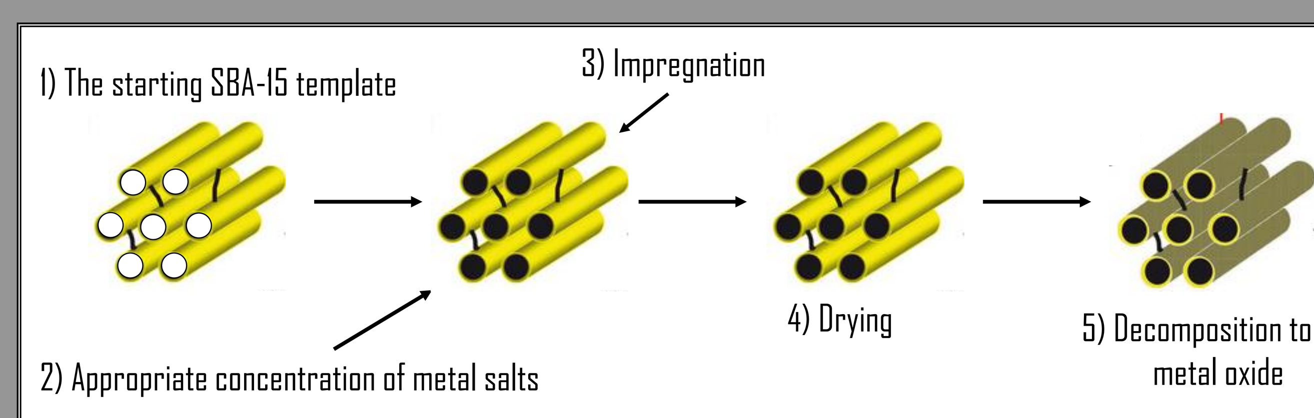




- Narrow distribution of pores diameter
- High-surface area (up to 1000 m^2/g)
- High percentage of hydroxyl groups on channels' walls
- Aptitude to modificate the surface properties
- Great chemical, thermal and mechanic stability

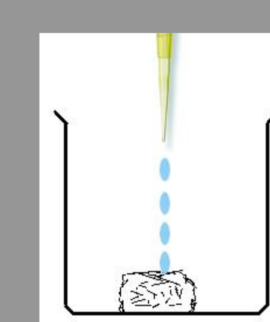
Sorbents preparation: The nanocompositing method

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



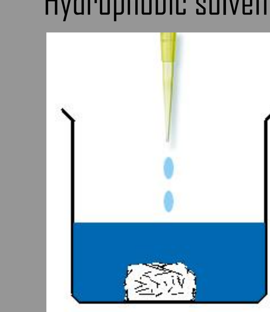
Impregnation strategies

Classic (one-solvent)
Incipient-wetness-impregnation



IWI_10
IWI_30
IWI_60

Innovative- Two-solvents
First suspended in *x* mL of Hydrophobic solvent



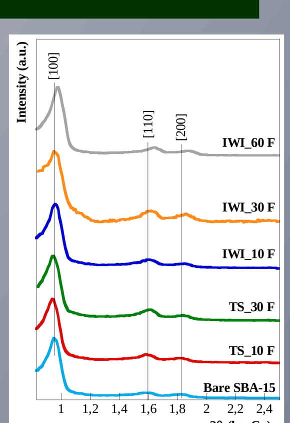
TS_10
TS_30

Ultrasonic bath treatment or stirring + Essication step + Calcination in air (minimun 500 °C)

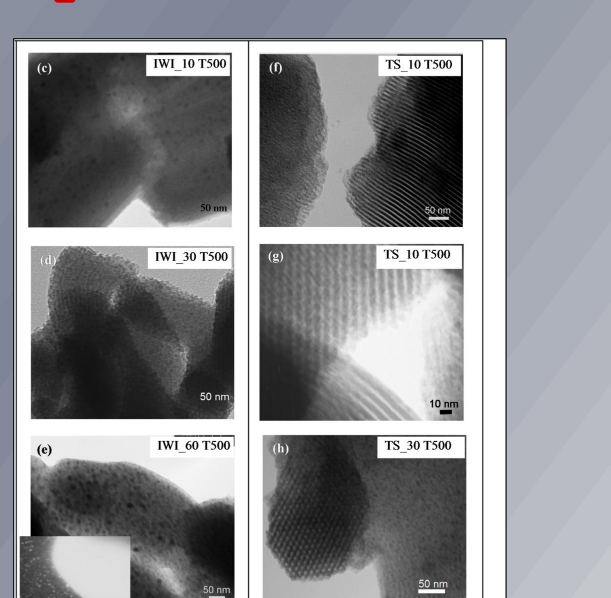
The Two-Solvents strategy leads to a better wettability and therefore increases the introduction of aqueous solutions into the pores, enhancing the dispersion of the metal oxide inside the pore network

Structural, morphological and textural features

Fresh

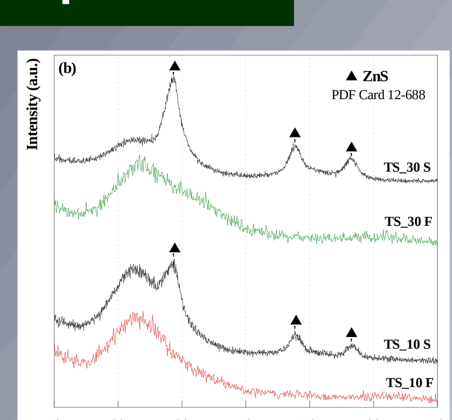


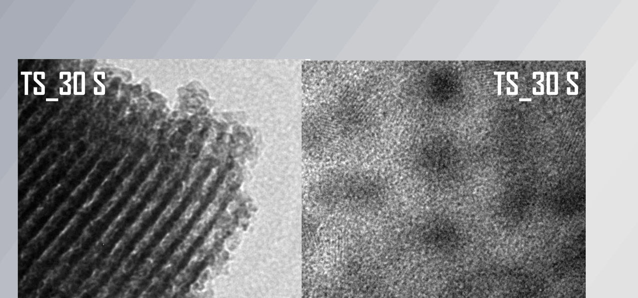
Hexagonal symmetry structure (spatial group *P6mm*) for all the composites. Shift towards higher 2Θ value for IWI_60 sample.



TEM analysis of the IWI-series samples reveal a good dispersion of the active phase into the support. In the case of the most concentrated sample (IWI_60), 10-20 nm zinc oxide nanoparticles larger than the pore size are also visible on the surface. The TS-series micrographs indicate a good dispersion of ZnO into the support and no presence of aggregates of large nanocrystals is revealed.

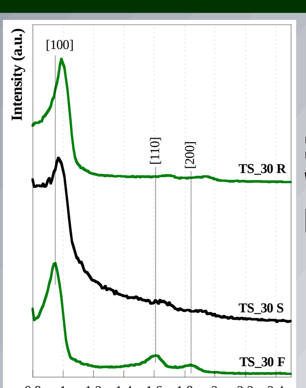
Sulphided





Three reflections (2Θ= 28.6°-47.7° e 56.6°) are easily assigned to ZnS phase. A rough estimation of the mean crystallite size by Debye-Scherrer equation, gives a value of **$\langle D \rangle_{XRD}$= 3-5 nm**. The support mesostructure is retained except for the IWI_60 sample (not shown).

Regenerated



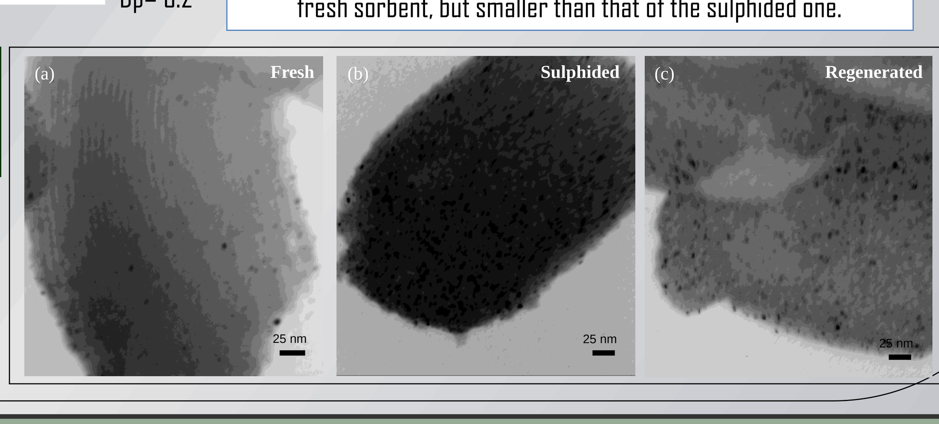
S_{BET}= 238
V_p= 0.58
Dp= 5.6

S_{BET}= 627
V_p= 0.7
Dp= 6.2

The Low-angle diffraction patterns reveals a progressive decrease shift toward higher angles: fresh > sulphided > regenerated, which suggest a progressive decrease in the pore size.

The fresh sample shows a low amount of small black spots (crystallite) indicating a low degree of ZnO crystallinity. In the sulphided sample both the number and size of the black spots increase visibly. In the regenereted sample the number of black spots is higher than that of the fresh one but lower than that of the sulphided sample; the size of the spots seems similar to that of the fresh sorbent, but smaller than that of the sulphided one.

Advanced hypothesis

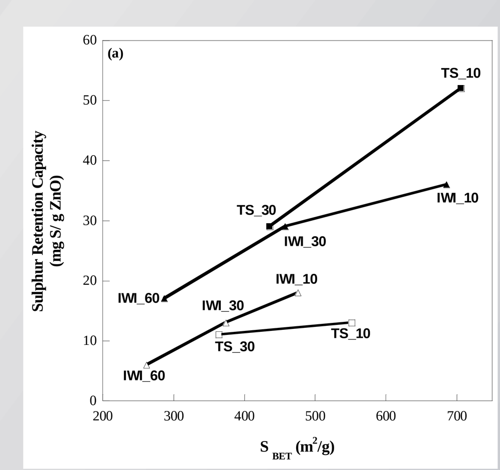


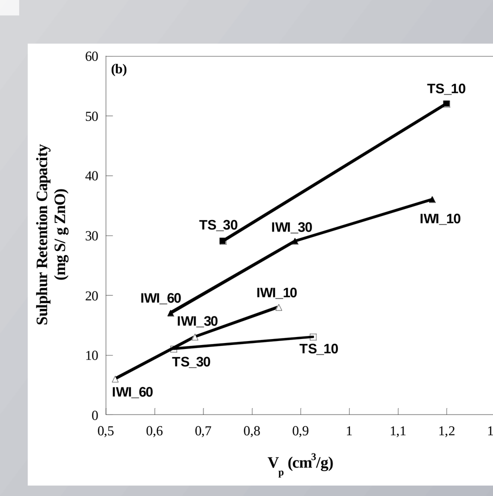
ZnO/SBA-15 Results

Desulphurisation test

$ZnO + H_2S \rightarrow ZnS + H_2O$

1) Quartz-made tubular reactor
2) Gaseous mixture at 1.5% vol. H_2S in He (0.3 mL/min H_2S)
3) In situ-activation with N_2 flow for 30 min at 300 °C (heating rate 20 °C/min)
4) Mass spectrometer (MS) + thermoconducibility detector (TCD)





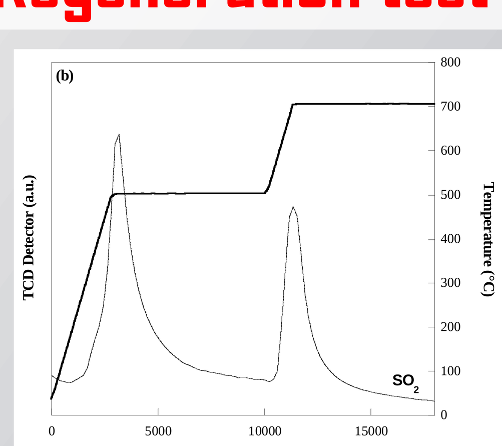
The data points cannot be interpolated by the same curve. Each set of points, as a function of preparation method (IWI or TS), requires a specific curve. The effectiveness of the active phase in the H_2S removal does not depend on the textural features only. The TS-series samples lie above that of the IWI-series, which suggest that the better way of exploiting the peculiar structure of SBA-15 is the use of Two-Solvents method for the confinement of the ZnO phase into its channels.

Sample	Calcination (°C)	B_t (s)	Retention Capacity (mg_S/g_{ZnO})	Retention Capacity ($mg_S/g_{sorbent}$)
Katalco$_{JM}$ 32-5	-	100	13	13.0
SBA-15	-	-	-	-
IWI_10	500	28	36	4.0
	600	14	18	1.8
IWI_30	500	66	29	9.0
	600	30	13	4.0
IWI_60	500	80	17	10.0
	600	27	6	3.6
TS_10	500	40	52	5.0
	600	10	13	1.3
TS_30	500	66	29	9.0
	600	26	11	3.4

The highest retention capacity per unit mass of ZnO is obtained for the TS_10 sample, followed by the IWI_10, both being much more higher than the corresponding value of the commercial ZnO sorbent. The high surface area support for disperding on a nanometric scale the active phase enhances the ability of the latter to react with the pollutant gas.

Regeneration test

$ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2$



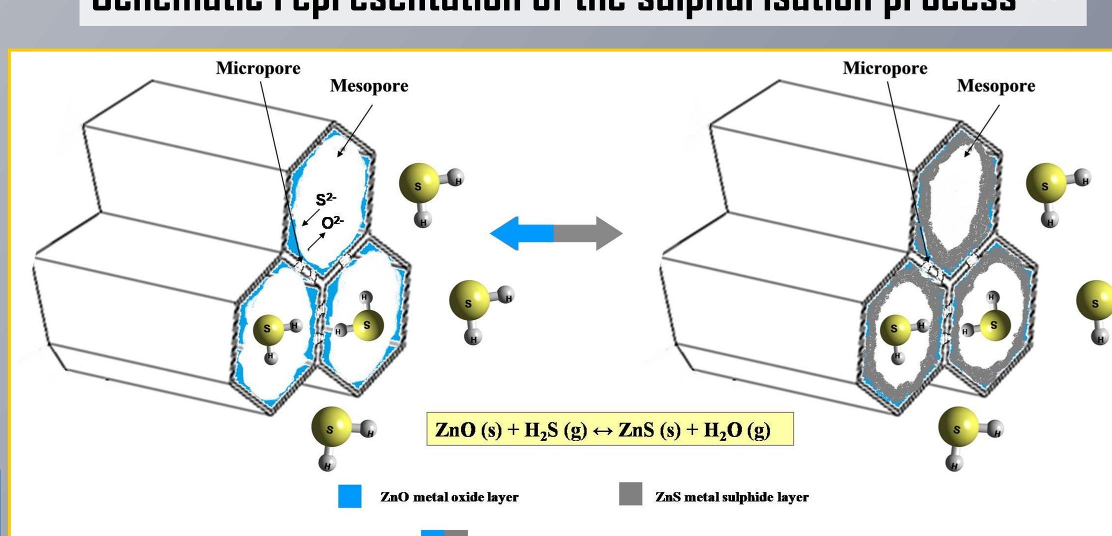
Sample	Run number[(a)]	B_t (s)	Retention Capacity (mg_S/g_{ZnO})	Retention Capacity ($mg_S/g_{sorbent}$)
Katalco$_{JM}$ 32-5	1	100	13	13
	2	25	3	3
	3	25	3	3
IWI_30_T500	1	66	29	9
	2	118	51	15
	3	135	59	18
TS_30_T500	1	66	29	9
	2	92	40	12
	3	95	41	12

(a) 1= fresh sorbent; 2 = after 1st regeneration; 3 = after 2nd

The TPO (Temperature-programmed oxidation) runs in flowing air show two peaks, corresponding to two different steps of SO_2 release. In view of the observed detrimental effect of the higher temperature on the sulphur retention capacity (see table above), it seems safer do not exceed 500 °C in the regeneration step.

Commercial sorbent shows poor regenerative capacity. ZnO/SBA-15 composites clearly show that the regeneration process enhances their performanc. Such improvement is maintaining during several cycles.

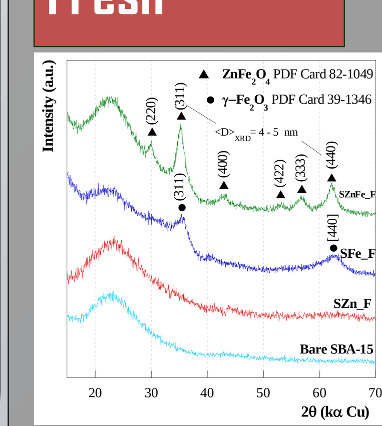
Schematic representation of the sulphurisation process [3]



Fe/SBA-15 and ZnFe/SBA-15 results

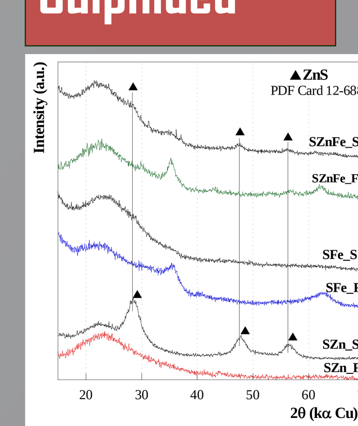
All Fe- and ZnFe-based composite sorbents were prepared via the Two-Solvents synthetic route with metal oxide loading of 20 wt. %

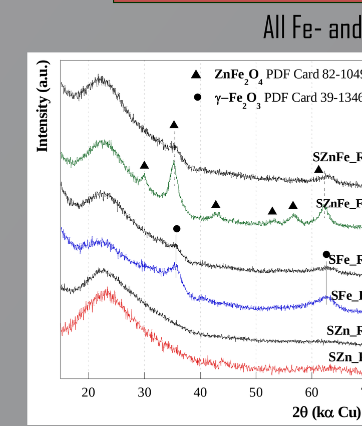
Fresh



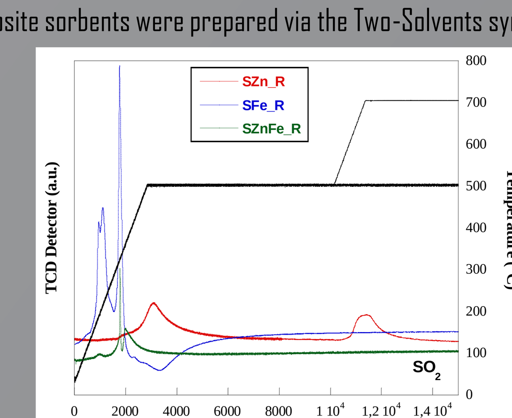
Zn_F shows only the typical haloes of amorphous silica. Fe_F composite exhibits two further bands attributed to the most intense reflections of maghemite-Fe_2O_3 phase. ZnFe_F exhibits a series of reflections ascribed to the cubic $ZnFe_2O_4$ spinel nanophase

Sulphided





Differently from the SZn_S sample, slight reflections attributable to ZnS phase can be also visible in the case of ZnFe_S. No reflections related to any iron sulphide phase were revealed in the SFe_S and SZnFe_S composites, suggesting a probably amorphous nature of the sulphided iron product. After regeneration at 500 °C the XRD reflections mainly attributable to the ZnS phase disappear and only diffraction peaks ascribable to Fe_2O_3 and $ZnFe_2O_4$ phases are observed in the Fe_R and ZnFe_R samples respectively.

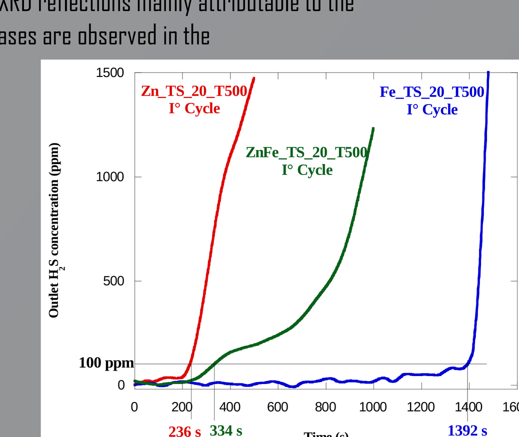


Regenerated

Comparison of regenerative TPO curves in the first cycle shows that for the Fe and ZnFe sorbents the regeneration temperature was much lower in respect to the Zn sorbent.

Preliminary H_2S sorption tests

Preliminary desulfurization breakthrough curves were obtained under the same operating conditions of sulfidation gas (20 ml/min composed of 1.5% H_2S) and sorbent bed configuration (100 mg of sorbent). Remarkable differences in the breakthrough time at 100 ppm were obtained.



Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	Breakthrough time (s)	Sulphur retention capacities (mg S/ g Active Phase)	Sulphur retention capacities (mg S/ g Sorbent)
Pure SBA-15	770	1.20	50	-	-
SZn_F	482	0.9087	178	52.73	10.54
SFe_F	576	0.8899	1346	400.86	80.17
SZnFe_F	493	0.9729	283	84.09	16.82

New H_2S nanocomposite sorbents consisting of different metal oxides supported into the SBA-15 silica were prepared by both conventional Incipient Wetness (only for ZnO) and Two-solvents impregnation techniques. Remarkable sulphur retention capacity, in the case of ZnO/SBA-15 composites, referred to the active phase was shown compared with a commercial sorbent. At variance with the case of the commercial product, the sorption properties are enhanced after regeneration and maintained upon repeating the sorption/regeneration cycle. The unexpected enhancement in the sulphur regeneration capacity has been ascribed to a reorganization of the active phase occurring during the first regeneration step. Different loading percentages of ZnO (10, 30, 60 wt.%) on SBA-15 and their characterization and H_2S sorption performance, have led to the best compromise for the choice of the loading of 20 wt.% for iron- and zinc ferrite-based sorbents. The XRD results indicate that the use of the iron in place of the zinc, inhibits the crystallization of the particles. Moreover, the experimental H_2S sorption data show that the presence of the iron significantly improves both desulphurization and regeneration activity compared to the zinc-based sorbent. Among the prepared sorbents, Fe_2O_3 composite gives the best performance during the first desulphurization cycle of hot coal gas under the adopted conditions. It is very important to observe that most of the sulphur was released within the temperature range of 220-350 °C against 500-690 °C of the zinc composites.

References **[1]** B.S. Liu, Z.Y. Wan, Y.P. Zhan, C.T. Au, *Fuel*, Vol. 98 (2012) 95-102. **[2]** **M. Mureddu**, I. Ferino, E. Rombi, M.G. Cutrufello, P. Deiana, A. Ardu, A. Musinu, G. Piccaluga, C. Cannas, *Fuel*, Vol. 102 (2012) 691-700. **[3]** **M. Mureddu**, I. Ferino, E. Rombi, M.G. Cutrufello, P. Deiana, A. Ardu, A. Musinu, G. Piccaluga, C. Cannas, *Renewable Energy Global Innovations* {ISSN 2291-2460} (2013) : http://reginnovations.org/