

MoS₂/ZnO Nanoparticles for H₂S Removal

Maria Sarno*, Eleonora Ponticorvo

Department of Industrial Engineering and Centre NANO_MATES, University of Salerno,
 Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy
msarno@unisa.it

MoS₂/ZnO nanoparticles (NPs) were synthesized by a one step, highly promising synthesis approach, to be tested for the effective removal of hydrogen sulfide from drilling mud. The syntheses were performed by thermolysis of ammonium thiomolybdates (NH₄)₂MoS₄ and zinc(II)acetylacetonate in a three necked flask under a flow of nitrogen. Zinc oxide NPs alone were also prepared. The samples were characterized by Raman Spectroscopy, Transmission (TEM-EDS) Electron Microscopy and X-ray diffraction (XRD). The synthesized NPs were used to remove hydrogen sulfide from water based drilling fluid. The efficiency of these NPs in the removal of hydrogen sulfide from drilling mud was evaluated and compared with that of ZnO NPs alone. The obtained results show that an amount of 3 g of MoS₂/ZnO NPs is able to remove 100% of H₂S (800 ppm) from water based drilling mud in just few minutes. On the other hand, 60 minutes are required in the case of 3 g of ZnO NPs alone.

1. Introduction

Large quantities of hydrogen sulfide (H₂S) are produced in gas and petroleum industries. It is a very toxic and corrosive gas, and it can be considered as a major source of air pollution (Duan et al., 2007; Ren et al., 2005; Haimour et al., 2005). According to the international environmental regulations H₂S contained in the acid gases should be effectively removed before emission to atmosphere. H₂S diffused into the drilling fluid is produced by sulfate reducing bacteria (SRB) in sea water or in formation water (connate water) under anaerobic conditions where the SRBs grow with organic materials such as crude oil as a substrate (Sandnes et al., 2002). Hydrogen sulfide is a colorless gas and low concentrations of it in air smell like rotten eggs. Its characteristic odor is perceptible in fresh air in a concentration of 0.002 mg/L of air. However the human sense of smell quickly becomes fatigued and may fail to give warning of higher concentration. Coma, collapse and death from respiratory failure may occur within a few seconds after one or two inspiration of the undiluted gas (Ferguson, 1975). H₂S can be present in drilling mud/water either as H₂S, HS⁻ or S⁻², depending on the pH value (Sandnes et al., 2002). To protect the health of drilling workers, the concentration of hydrogen sulphide above the fluid, emitted due to the partial pressure of the gas, is less than about 15 ppm (Davidson, 2004). Various adsorbents have been used in industry to remove H₂S from different media (Li et al., 2006; Ros et al., 2007). Zinc compounds such as zinc oxide (ZnO) and zinc carbonate are common scavengers to remove H₂S from drilling fluids (Davidson, 2004). ZnO is a commodity sorbent and good candidate for the removal of H₂S in drilling fluids, because its high zinc content (80 %) and has well predictable reaction kinetics and absorption capacity. It is also readily available compared with other sorbents, such as molecular sieves or zinc-titanium oxide. However, the system using suspended catalyst particles requires a separation step to recover the catalysts. In this case, suitable techniques of high cost such as centrifugation or filtration steps are necessary. On the other hand, the adsorption and dissociation of hydrogen on molybdenum-base catalysts has been the subject of several studies (Kalapala, 2014; Alexiev et al., 2001; Cristol et al., 2002; Travert et al., 2002).

In this work, considering the very high porosity of the nanomaterials, which results in an high surface area and a faster scavenge of H₂S than bulk materials, MoS₂/ZnO nanoparticles (NPs) were synthesized by a one step, highly promising synthesis approach (Altavilla et al., 2013; Sarno et al., 2017a). The multifunctional nanoparticles, obtained by thermolysis of suitable precursors in organic solvent, were characterized by the combined use of different techniques. Raman Spectroscopy, Transmission Electron

Microscopy (TEM) and X-ray diffraction (XRD) were employed. The efficiency of these nanoparticles in the removal of hydrogen sulfide from drilling mud was evaluated and also compared with that of zinc oxide alone.

2. Experimental

The synthesis was carried out using standard airless procedures and commercially available reagents above described (Sarno et al., 2014a; Sarno et al., 2016, Sarno et al., 2017b). For the synthesis of ZnO nanoparticles covered by MoS₂: 2.5 mmol of zinc(II)acetylacetonate, 1 mmol of ammonium tetrathiomolybdate, 10 mmol of 1,2-hexadecanediol, 6 mmol of oleic acid, 6 mmol of oleylamine, and 20 mL of benzyl ether, were used. The mixtures put in a three necked flask, magnetically stirred under a flow of nitrogen, were heated to 200 °C for 2 h and then heated to reflux (~300 °C) for 1 h. Ethanol (40 mL) and hexane (30 mL) were used during post synthesis steps for purification (Sarno et al., 2016, Sarno et al., 2017b). 1.5 g of sodium sulfide nonahydrate (equivalent of about 800 ppm H₂S) were added to 128 mL of water based drilling mud and 128 mL of water. The so obtained slurry was homogenized by stirring for 20 min. Different tests were performed adding 3 or 2 g of nanoparticles, 40 mL of the slurry were taken out to be used as blank. At time zero and at different times, samples were taken out from the slurry to be analysed by gas chromatography. The experiment was carried out for MoS₂/ZnO nanoparticles and zinc oxide alone (prepared in the same operating condition but tetrathiomolybdate). The sampling was done after about 5, 10, and 30 min, respectively.

3. Results and discussion

Typical TEM images of the ZnO and MoS₂/ZnO are shown in Figure 1. Both samples are constituted of nanoparticles with small size NPs, ~18 nm for ZnO and 20 nm for MoS₂/ZnO that in particular are covered by MoS₂ nanosheets as evidenced in the Figure 1c.

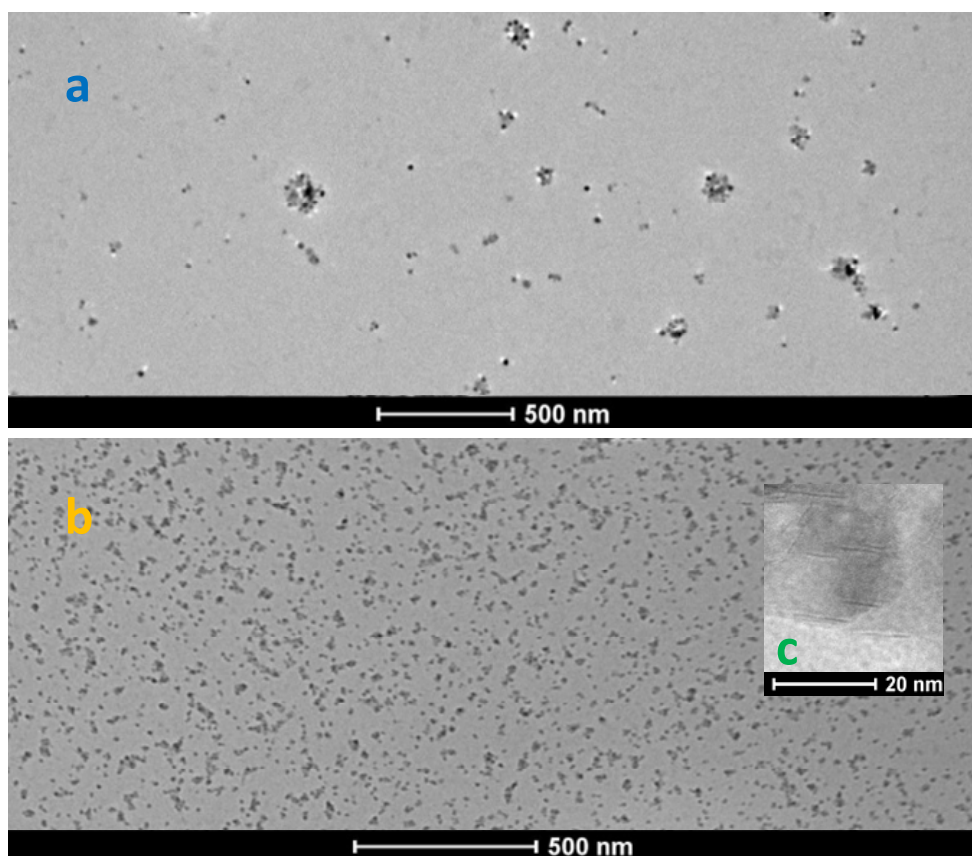


Figure 1 TEM images of ZnO (a) and MoS₂/ZnO (b,c).

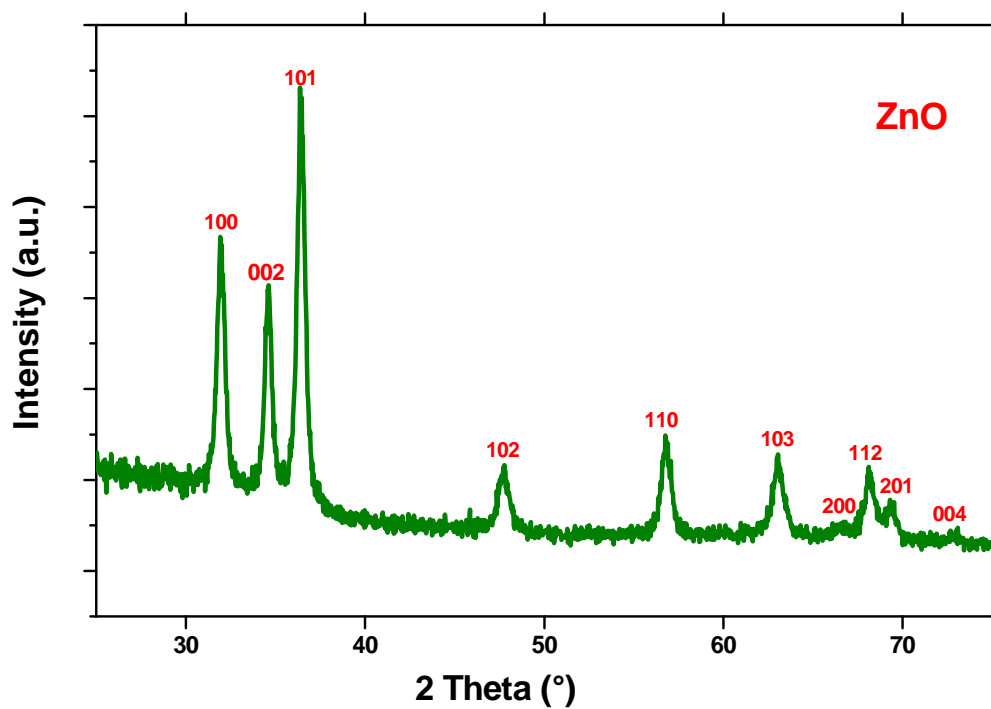


Figure 2. XRD Spectrum of ZnO.

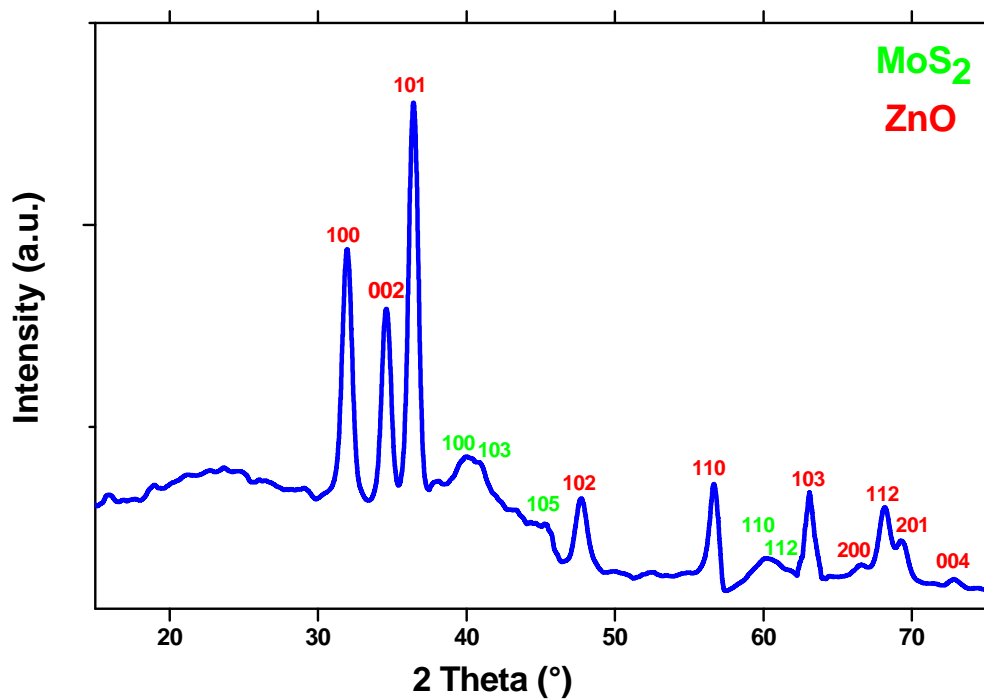


Figure 3. XRD Spectrum of MoS₂/ZnO.

The crystal structure of ZnO NPs was characterized by XRD with Cu K α radiation. Figure 2 shows XRD patterns of ZnO NPs. The peaks at $2\theta = 31.63^\circ, 34.30^\circ, 36.11^\circ, 46.80^\circ, 55.51^\circ, 62.13^\circ, 65.26^\circ, 66.99^\circ, 68.93^\circ,$ and 73.01° were assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) of ZnO NPs (Nikazar et al., 2014), indicating that polycrystalline wurtzite structure (Zincite, JCPDS 5-0664) was obtained. No peaks from any impurities were detected, indicating high purity ZnO NPs. The average crystallite size of ZnO NPs estimated by Scherrer's formula was found to be 17.8 ± 4.56 nm.

Figure 3 shows XRD patterns of MoS₂/ZnO NPs. In addition to the peaks of ZnO, the typical peaks of MoS₂ can be seen. In particular, it is possible to assign the reflection peaks of the family lattices planes (100), (103), (105), (110) and (112) of MoS₂ (JCPDS 17-0744).

The Raman spectrum of MoS₂/ZnO nanoparticles is shown in Figure 4. Intense bands at 380 cm^{-1} and 402 cm^{-1} are assigned to E_{2g} and A_{1g} modes of MoS₂, the band at 436 cm^{-1} is attributed to ZnO non-polar optical phonons E₂ mode (Guan et al., 2017). It has been found (Lee et al., 2010) that the frequency difference between the two most prominent Raman bands depends monotonically on the number of MoS₂ layers. The frequency difference in cm^{-1} of the A_{1g} and E_{2g} modes for MoS₂ indicates that most of the sheets have a number of layers between 2 and 4 (Sarno et al., 2014b).

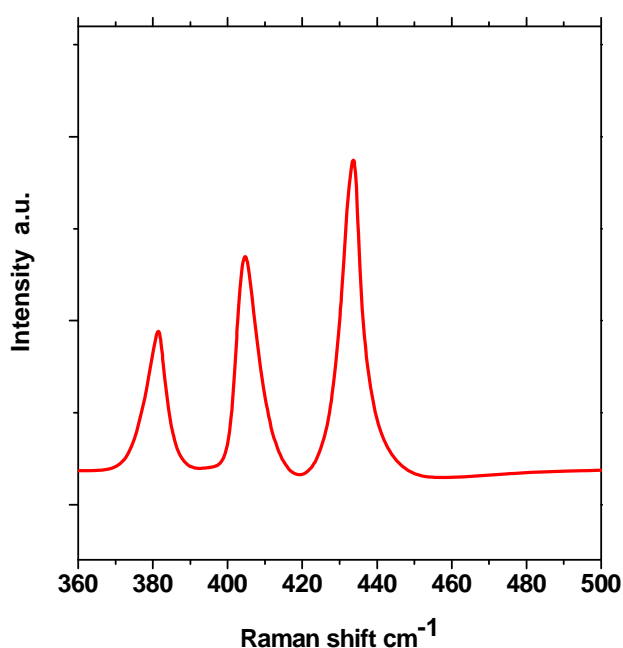


Figure 4. Raman Spectrum of MoS₂/ZnO

Starting from an initial concentration of 800 ppm, the amounts of scavenged H₂S by ZnO and MoS₂/ZnO nanoparticles in water-base drilling mud are shown in Figure 5. The amount of scavenged hydrogen sulphide after 60 min is 100 % for ZnO. On the other hand, MoS₂/ZnO completely remove H₂S from mud after ~16 min. Moreover, the results in Figure 5 permit to compare experiments with different amount of absorbent, that in the case of MoS₂/ZnO results lower. When using 3 g of MoS₂/ZnO, the removal of 100% H₂S requires ~10 min.

Thus, there is a remarkable difference between the rates of H₂S adsorption on bare ZnO and MoS₂/ZnO nanoparticles. ZnO has also been used as an effective scavenger for removing soluble sulfides from oil-based muds (Garrett et al., 1988), so MoS₂/ZnO, with its higher efficiency, can be proposed too. The obtained results show that, MoS₂/ZnO nanoparticles are reliable scavengers to effectively remove H₂S from drilling fluids.

Superior performance of MoS₂/ZnO in the elimination of H₂S will decrease consumption of bulk ZnO, which will result in minimizing the environmental pollution and lower consumption of natural resources. On the other hand, quantitative evaluations, specific grams of H₂S adsorbed, require the analysis of the formed sulfides, whose presence although certainly low in the test conditions cannot be completely neglected.

H₂S removal on ZnO NPs surface proceeds through the follow known reaction:



On the other hand, MoS₂ nanosheets, stabilizing ZnO against aggregation, because of the large number of exposed edges, supplies further active sites for H₂S adsorption/decomposition, which follows a SH_{ads}⁻ and H_{ads}⁺ mediated mechanism (Startsev, 2017), evolving in the release of S₂(gas).

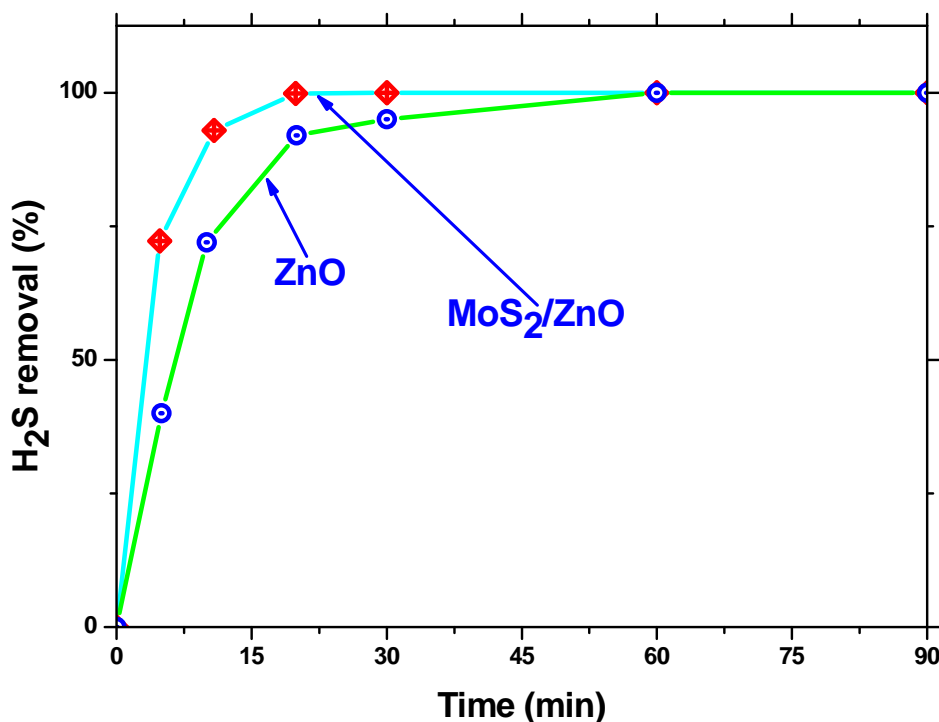


Figure 5. Comparison of H₂S amount removed by ZnO (in green and blue) 3 g in batch and MoS₂/ZnO (in cyan and red) 2 g in batch.

4. Conclusions

TEM images evidence the nanoparticles nature of the produced materials, small size NPs, ~18 nm for ZnO and 20 nm for MoS₂/ZnO mean diameters were obtained, respectively. In particular, at increasing magnification results evident that the apparent higher size of the MoS₂/ZnO NPs is due to the MoS₂ nanosheets covering the quasi-spherical nanoparticles of ZnO.

The MoS₂/ZnO formation was confirmed by XRD analysis. The frequency difference in cm⁻¹ of the A_{1g} and E_{2g} modes for MoS₂ indicates that most of the sheets, laying on ZnO, have a number of layers between 2 and 4.

MoS₂/ZnO completely removed H₂S from mud after ~ 16 min. Moreover, the results permit to compare experiments with different amount of absorbent, that in the case of MoS₂/ZnO results lower. When using 3 g of MoS₂/ZnO, the removal of 100% H₂S requires ~ 10 min. MoS₂/ZnO nanoparticles are reliable scavengers to effectively remove H₂S and soluble sulfides from drilling fluids. Superior performance of MoS₂/ZnO in the elimination of H₂S will decrease consumption of bulk ZnO, which will result in minimizing the environmental pollution and lower consumption of natural resources. The obtained results show that the synthesized nanoparticles are able to remove hydrogen sulfide from water based drilling mud in just few minutes.

References

Alexiev V., Prins R., Weber T., 2001, DFT study of MoS₂ and hydrogen adsorbed on the (1010) face of MoS₂, Physical Chemistry Chemical Physics, 3, 5326-5336.

- Altavilla C., Sarno M., Ciambelli P., Senatore A., Petrone V., 2013, New 'chimie douce' approach to the synthesis of hybrid nanosheets of MoS₂ on CNT and their anti-friction and anti-wear properties, *Nanotechnology*, 24, 125601-11pp.
- Cristol S., Paul J.F., Payen E., Bougeard D., Clemendot S., Hutschka F., 2002, Theoretical Study of the MoS₂ (100) Surface: A Chemical Potential Analysis of Sulfur and Hydrogen Coverage. 2. Effect of the Total Pressure on Surface Stability, *The Journal of Physical Chemistry B*, 106, 5659-5667.
- Davidson E., 2004, Method and composition for scavenging sulphid in drilling fluids., U.S. Patent: 6476611.
- Duan Z., Sun R., Liu R., Zhu C., 2007, Accurate thermodynamic model for the calculation of H₂S solubility in pure water and brines, *Energy & Fuels*, 21, 2056-2065.
- Ferguson P.A., 1975, Hydrogen sulfide removal from gases, air, and liquids, Noyes Data corporation, new Jersey, USA.
- Garrett R.L., Carlton L.A., Denekas M.O., 1988, Methods for field monitoring of oil- based drilling fluids for hydrogen sulfide and water intrusions, *SPE Drilling Engineering*, 3, 296-302.
- Guan Z., Wang P., Li Q., Li Y., Fu X., Yang., 2017, Remarkable enhancement in solar hydrogen generation from MoS₂-RGO/ZnO composite photocatalyst by constructing a robust electron transport pathway, *Chemical Engineering Journal*, 327, 397-405.
- Haimour N., El-Bishtawi R., Ail-Wahbi A., 2005, Equilibrium adsorption of hydrogen sulfide onto CuO and ZnO, *Desalination*, 181, 145-152.
- Kalapala S., 2014, Removal of Hydrogen Sulfide from Landfill Gas Using a Solar Regenerable Adsorbent, PhD Thesis, Youngstown State University, Youngstown, OH, USA.
- Lee C., Yan H., Brus L.E., Heinz T.F., Hone J., Ryu S., 2010, Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂, *ACS Nano*, 4, 2695-2700.
- Li L., King D.L., 2006, H₂S removal with ZnO during fuel processing for PEM fuel applications, *Catalysis Today*, 116, 537-541.
- Nikazar M., Alizadeh M., Lalavi R., Rostami M.H., 2014, The optimum conditions for synthesis of Fe₃O₄/ZnO core/shell magnetic nanoparticles for photodegradation of phenol, *Iranian Journal of Environmental Health Science & Engineering*, 12, 21-6pp.
- Ren C., Liu D., Bai Z., Li T., 2005, Corrosion behavior of oil tube steel in simulant solution with hydrogen sulfide and carbon dioxide, *Mater. Chem. phys.*, 93, 305-309.
- Ros A., Lillo-Rodenas M.A., Canals-Batlle C., Fuente E., Montes-Moran. M.A., Martin M.J., Linares-Solano A., 2007, A new generation sludge-based Adsorbent for H₂S abatement at room temperature, *Environmental Science & Technology*, 41, 4375-4381.
- Sandnes E.S., Hundvag H.O., 2002, Removal of H₂S in drilling mud, U.S. Patent: 6365053 B1.
- Sarno M., Cirillo C., Ciambelli P., 2014a, Selective graphene covering of monodispersed magnetic nanoparticles, *Chemical Engineering Journal*, 246, 27-38.
- Sarno M., Garamella A., Cirillo C., Ciambelli P., 2014b, MoS₂ Nanosheets for HER and LIB, *Chemical Engineering Transactions*, 41, 391-396.
- Sarno M., Ponticorvo E., 2017a, Effect of the amount of nickel sulphide, molybdenum disulphide and carbon nanosupport towards Tafel Slope and overpotential optimization, *Nanotechnology*, 28, 214003-8pp.
- Sarno M., Ponticorvo E., Cirillo C., Ciambelli P., 2016, Magnetic nanoparticles for PAHs solid phase extraction, *Chemical Engineering Transactions*, 47, 313-318.
- Sarno M., Ponticorvo E., Cirillo C., Ciambelli P., 2017b, Polycyclic Aromatic Hydrocarbons Extraction Based on Graphene Coated Magnetic Alloy Nanoparticles, *Chemical Engineering Transactions*, 60, 145-150.
- Startsev A.N., 2017, The Reaction Mechanisms of H₂S Decomposition into Hydrogen and Sulfur: Application of Classical and Biological Thermodynamics, *Journal of Thermodynamics & Catalysis*, 8, 1000186-8pp.
- Travert A., Nakamura H., van Santen R.A., Cristol S., Paul J.F., Payen E., 2002, Hydrogen Activation on Mo-Based Sulfide Catalysts, a Periodic DFT Study, *Journal of the American Chemical Society*, 124, 7084-7095.