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MoS_2/ZnO Nanoparticles for H_2S Removal

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MoS_2/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 $(NH_4)_2MoS_4$ 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 MoS_2/ZnO NPs is able to remove 100% of H_2S (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 (H_2S) 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 H_2S contained in the acid gases should be effectively removed before emission to atmosphere. H_2S 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). H_2S can be present in drilling mud/water either as H_2S, 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 H_2S 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 H_2S from drilling fluids (Davidson, 2004). ZnO is a commodity sorbent and good candidate for the removal of H_2S 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 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 H_2S than bulk materials, MoS_2/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 MoS_2: 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 MoS_2/ZnO are shown in Figure 1. Both samples are constituted of nanoparticles with small size NPs, ~18 nm for ZnO and 20 nm for MoS_2/ZnO that in particular are covered by MoS_2 nanosheets as evidenced in the Figure 1c.

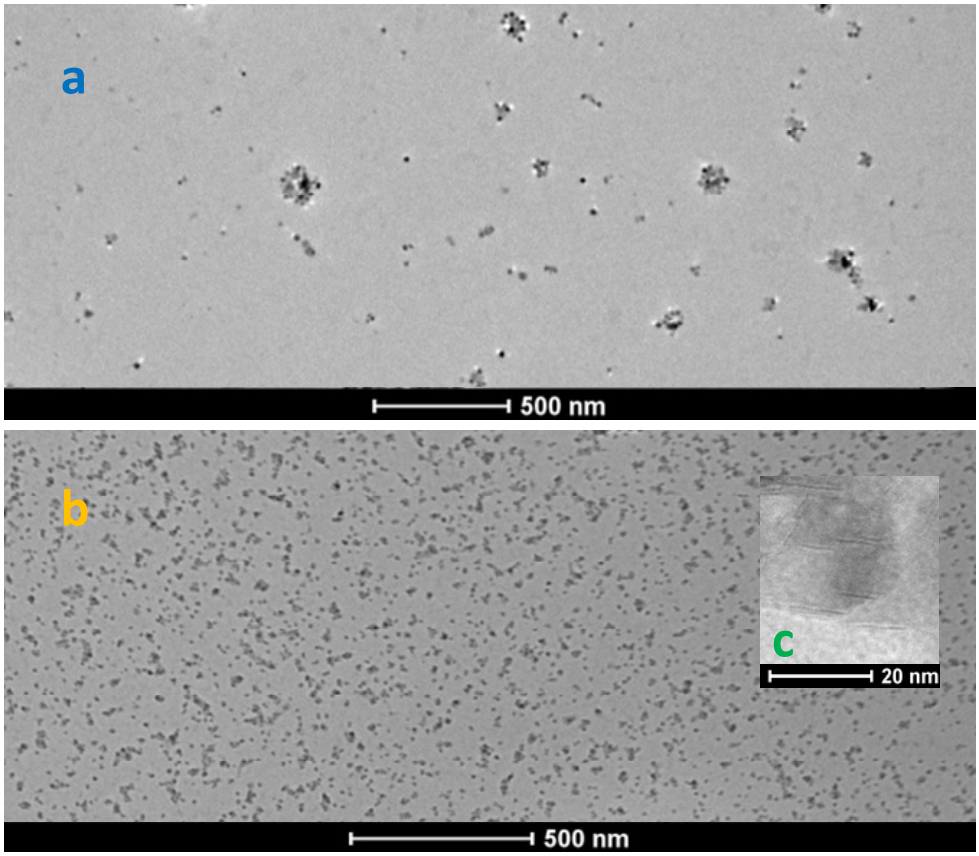

Figure 1 TEM images of ZnO (a) and MoS_2/ZnO (b,c).

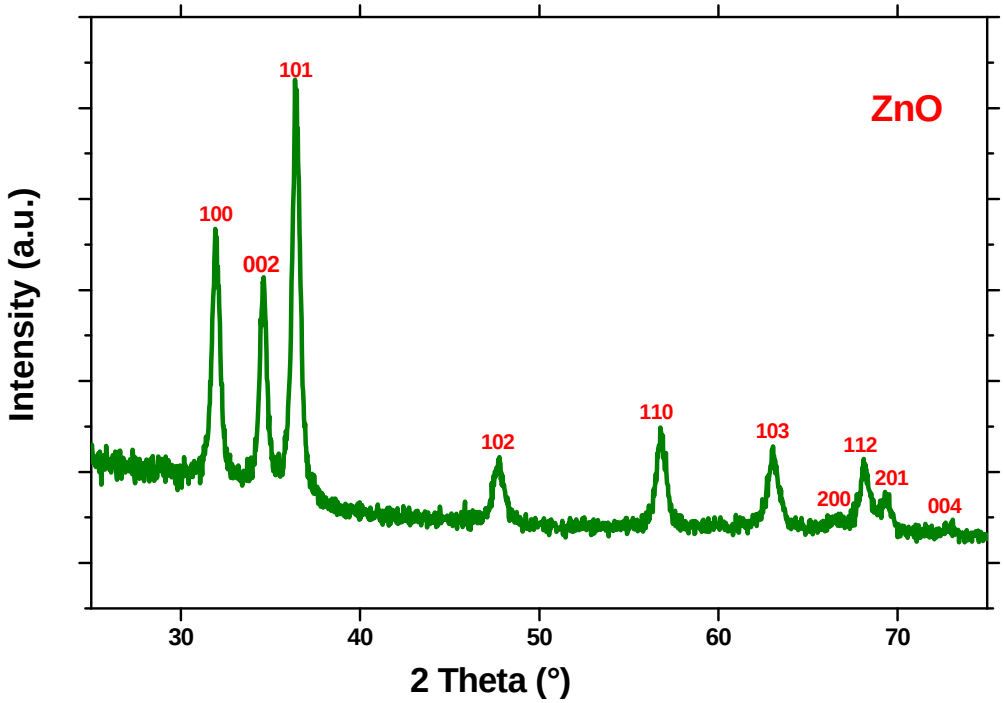

Figure 2. XRD Spectrum of ZnO.

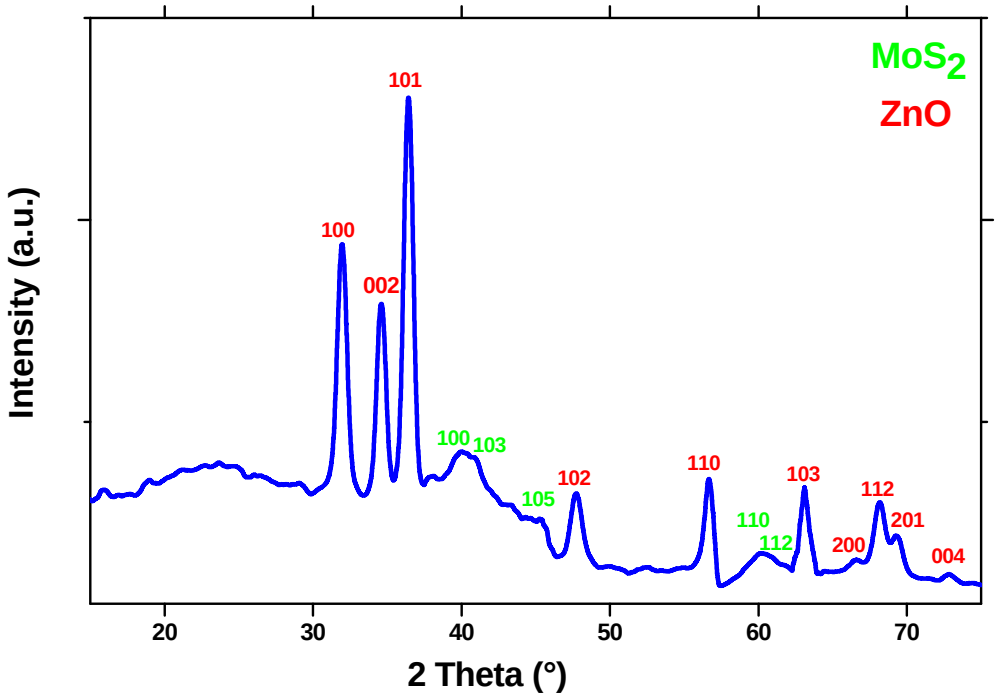

Figure 3. XRD Spectrum of MoS_2/ZnO.

The crystal structure of ZnO NPs was characterized by XRD with Cu Kα radiation. Figure 2 shows XRD patterns of ZnO NPs. The peaks at 2θ = 31.63°, 34.30°, 36.11°, 46.80°, 55.51°, 62.13°, 65.26°, 66.99°, 68.93°, 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 MOS_2/ZnO NPs. In addition to the peaks of ZnO, the typical peaks of MoS_2 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 MoS_2 (JCPDS 17-0744) .

The Raman spectrum of MoS_2/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 MoS_2, the band at 436 cm^{-1} is attributed to ZnO non-polar optical phonons E_2 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 MoS_2 layers. The frequency difference in cm^{-1} of the A_{1g} and E_{2g} modes for MoS_2 indicates that most of the sheets have a number of layers between 2 and 4 (Sarno et al., 2014b).

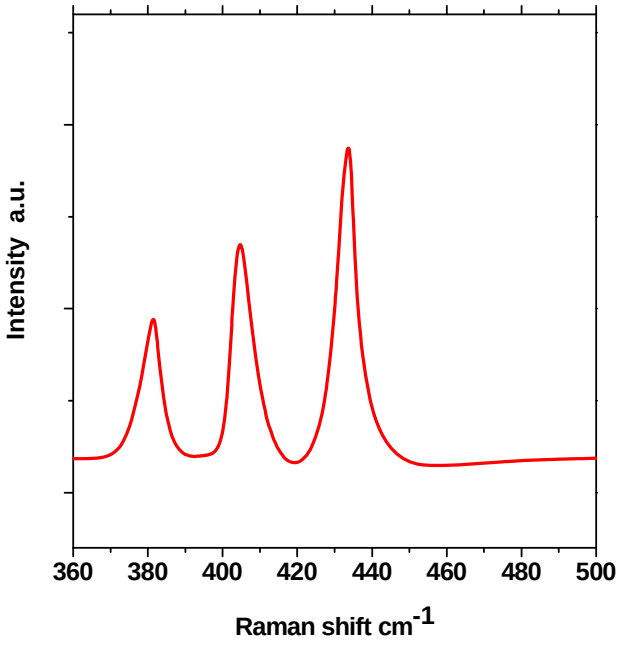

Figure 4. Raman Spectrum of MoS_2/ZnO

Starting from an initial concentration of 800 ppm, the amounts of scavenged H_2S by ZnO and MoS_2/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, MoS_2/ZnO completely remove H_2S 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 MoS_2/ZnO results lower. When using 3 g of MoS_2/ZnO, the removal of 100% H_2S requires ~10 min.

Thus, there is a remarkable difference between the rates of H_2S adsorption on bare ZnO and MoS_2/ZnO nanoparticles. ZnO has also been used as an effective scavenger for removing soluble sulfides from oil-based muds (Garrett et al., 1988), so MoS_2/ZnO, with its higher efficiency, can be proposed too. The obtained results show that, MoS_2/ZnO nanoparticles are reliable scavengers to effectively remove H_2S from drilling fluids..

Superior performance of MoS_2/ZnO in the elimination of H_2S 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 H_2S adsorbed, require the analysis of the formed sulfides, whose presence although certainly low in the test conditions cannot be completely neglected.

H_2S removal on ZnO NPs surface proceeds through the follow known reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (1)$$

On the other hand, MoS_2 nanosheets, stabilizing ZnO against aggregation, because of the large number of exposed edges, supplies further active sites for H_2S adsorption/decomposition, which follows a SH^-_{ads} and H_{ads} mediated mechanism (Startsev, 2017), evolving in the release of S_2(gas).

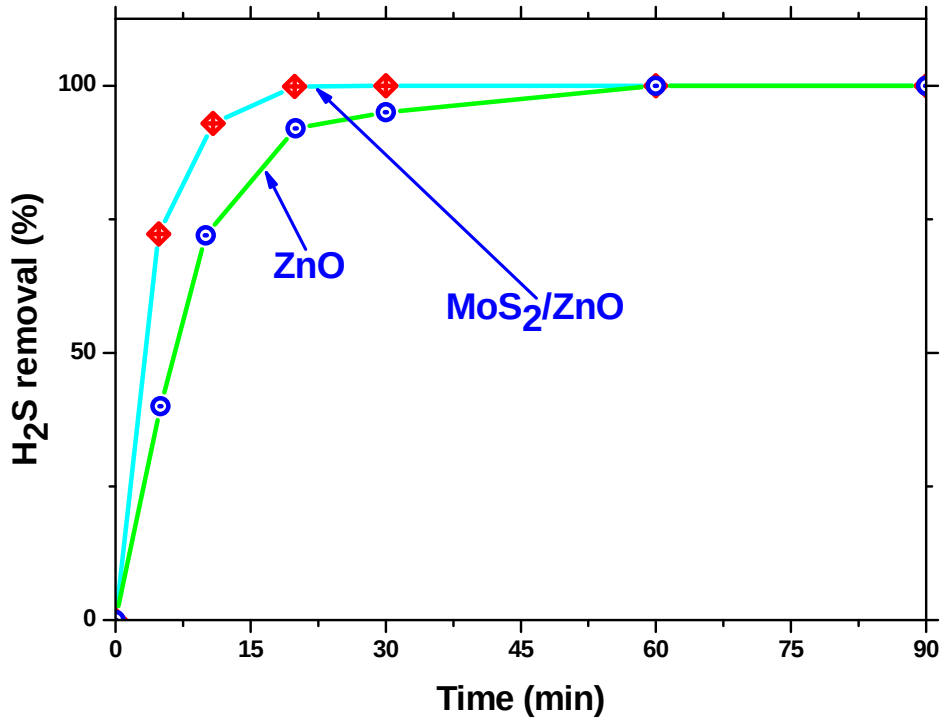

Figure 5. Comparison of H_2S amount removed by ZnO (in green and blue) 3 g in batch and MoS_2/ZnO (in cyan and red) 2 g in batch.

4. Conclusions

TEM images evidence the nanoparticles nature of the produced materials, small size NPs, ~18 nm for ZnO and 20 nm for MoS_2/ZnO mean diameters were obtained, respectively. In particular, at increasing magnification results evident that the apparent higher size of the MoS_2/ZnO NPs is due to the MoS_2 nanosheets covering the quasi-spherical nanoparticles of ZnO.

The MoS_2/ZnO formation was confirmed by XRD analysis. The frequency difference in cm^{-1} of the A_{1g} and E_{2g} modes for MoS_2 indicates that most of the sheets, laying on ZnO, have a number of layers between 2 and 4.

MoS_2/ZnO completely removed H_2S from mud after ~ 16 min. Moreover, the results permit to compare experiments with different amount of absorbent, that in the case of MoS_2/ZnO results lower. When using 3 g of MoS_2/ZnO, the removal of 100% H_2S requires ~ 10 min. MoS_2/ZnO nanoparticles are reliable scavengers to effectively remove H_2S and soluble sulfides from drilling fluids. Superior performance of MoS_2/ZnO in the elimination of H_2S 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.

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