

# Solvent Selection in Impregnation of Zinc Oxide Nanoparticles into MCM-41 Investigation of Its Ability Toward H<sub>2</sub>S Removal from Crude Oil

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## Abstract

Silicate mesoporous materials are of the main interesting adsorbents for decreasing of hydrogen sulfide (H<sub>2</sub>S) from crude oil. In this work zinc impregnated highly ordered MCM-41 was synthesized via post-synthesis functionalization and was used as adsorbent for removal of H<sub>2</sub>S from crude oil. Also the variation of solvents was mainly adjusted. In order to determine the ideal solvent for the synthesis of zinc incorporated MCM-41, a few solvents (water, ethanol and THF) has been tried in these experiments. The experiments showed that THF is a better solvent to get better materials.

*Keywords:* MCM-41; ZnO Nanoparticle; solvent; H<sub>2</sub>S removal; Crude oil

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## 1. Introduction

Mesoporous silicas are one of the best-known and most widely applied porous materials. Since the discovery of MCM-41, the researches dealing with the controlled design of porous materials with nanometer scale periodicity have expanded rapidly. Unlike previous mesoporous silica, MCM-41 has ordered and well-defined pore structures with narrow pore size distributions [1, 2]. The pore size of MCM-41 is large enough to accommodate a variety of large molecules, that's why it is extensively used as adsorbents, catalysts and catalyst supports owing to its high surface areas and site accessibility [3-5]. Besides variable pore diameters and large surface areas, MCM-41 contain different types of silanol groups, i.e. external surface, internal surface silanol group which can be functionalized by functional groups. The silanol groups present at the surface of the walls are suitable for chemical bonding of organic ligands or anchoring inorganic species. [6]. In one way functionality is directly introduced via reaction of silanol

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groups and in another way, a transition metal, metal oxide or a bimetal complex is grafted on the wall without the use of intermediate silane complexing agent. Then the surface hydroxyl groups can directly react with the metal species.

As MCM-41 offers a relatively large pore volume, impregnation appears to be a suitable method for the application of precursors of active phase(s) inside the mesopores. A number of methods have grown for the application of active phases on these types of support materials. The most frequently applied preparation method is impregnation. The major advantage of this method is its simplicity [7].

During impregnation a suitable support material is contacted with a solution containing a precursor of the active phase. Upon drying of the support material after impregnation solvent is evaporated and as a result the precursor of the active phase adheres to the surface of the support. Prior to impregnation support materials are frequently shaped into robust bodies, which facilitate their handling. Because of the shaping process pores are generated between the primary particles of support material and upon impregnation these pores are filled with precursor solution. Precursor solution in impregnation method contains metal solid dissolved in an applicable solvent, a useful property for selection of solvents is their solubility parameters. So the solvent selection is effective on the samples final structure. In the impregnation preparation water is the most used solvent. Herein three solvents are applied and their influence on the structure will be discussed.

In this work zinc oxide nanoparticles were incorporated on MCM-41 in order to have hydrogen sulfide adsorbent. One of the main interesting methods of decreasing of  $H_2S$  is using silicate mesoporous materials as based materials as adsorbent [3, 8]. Also from the thermodynamic analysis, it is been shown that zinc oxide is a good adsorbent for having high sulfur removal efficiency because of high equilibrium constant. Moreover, ZnO is considered a cost-effective and stable sorbent compared to other metal oxides [9].

Sulfur-containing compounds in middle distillate fuels are known to have negative impacts on the environment because of SO<sub>x</sub> emission from their combustion exhaust products, and the associated contribution to acid rain. Beside its environmental hazards, hydrogen sulfide causes extensive corrosion in refinery plants [10]. Due to the ever increasing standards of efficiency required by environmental protection, decreasing of  $H_2S$  of crude oil has become more and more important.

## 2. Materials and methods

### 2.1. Synthesis

All chemicals were purchased from Merck and used without further purification. In a typical synthesis, cetyltrimethyl-ammonium bromide (CTAB) and NaOH were dissolved in water. While stirring, tetraethylorthosilicate (TEOS) was added to this solution over a period of 15 min. After 70-min stirring, the obtained suspension was transferred into the Teflon-lined stainless steel and autoclaved at 90°C for 96 h. Then, the precipitate was filtered and washed with deionized water and acetone, respectively. The as-synthesized samples were calcined in heating rate of 1°C/min up to 550°C and held at this temperature for 5 h.

For the preparation of zinc-containing MCM-41, 2 grams of MCM-41 was impregnated with  $Zn(NO_3)_2 \cdot 4H_2O$  in 100 mL of 3 different solvents water, ethanol and tetrahydrofuran (THF). The suspensions were shaken for 24 hours and dried under vacuum at 80°C and calcined at 550°C for 3 hours. The weight percent of zinc in the corresponding samples was 10.

Resultant samples denoted as  $ZnO_W/MCM$ ,  $ZnO_E/MCM$  and  $ZnO_T/MCM$  where W, E and T specifies respectively water, ethanol and THF, the used solvent in the synthesis of corresponding sample.

### 2.2. Characterization

Synthesized samples were characterized using XRD, nitrogen physisorption, SEM and HRTEM. Determination of  $H_2S$  were carried out via UOP-163 standard test method using METTLER TOLEDO G20 apparatus.

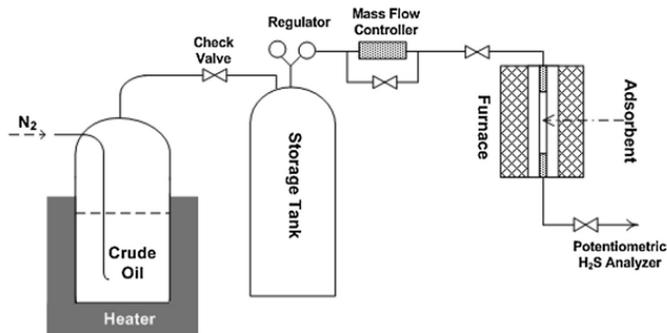


Fig. 1: Schematic representation of laboratory-made H<sub>2</sub>S adsorption apparatus.

### 2.3. H<sub>2</sub>S adsorption

Soumar crude oil was obtained from south of Iran. At first, H<sub>2</sub>S of crude oil was removed using hot stripping. The concentration of H<sub>2</sub>S in the crude oil was lower than 1 ppm. The concentration of H<sub>2</sub>S in the H<sub>2</sub>S-in-LPG was 5,000 ppm. This concentration was taken as the criterion for the H<sub>2</sub>S break point during adsorption of H<sub>2</sub>S.

Adsorption measurements for H<sub>2</sub>S were performed using a laboratory-made apparatus. Figure 1 illustrates the adsorption apparatus made and used in this work. Analysis of the reactor effluent stream using UOP163 method gave H<sub>2</sub>S break point curves.

## 3. Results and discussion

### 3.1. XRD analysis

All prepared samples were characterized using low- and high-angle X-ray diffraction to get structural information about their pore order and phases of the obtained zinc oxide, respectively.

X-ray diffraction patterns of ZnO<sub>T</sub>/MCM, ZnO<sub>W</sub>/MCM and ZnO<sub>E</sub>/MCM are shown in figure 2a, b and c respectively.

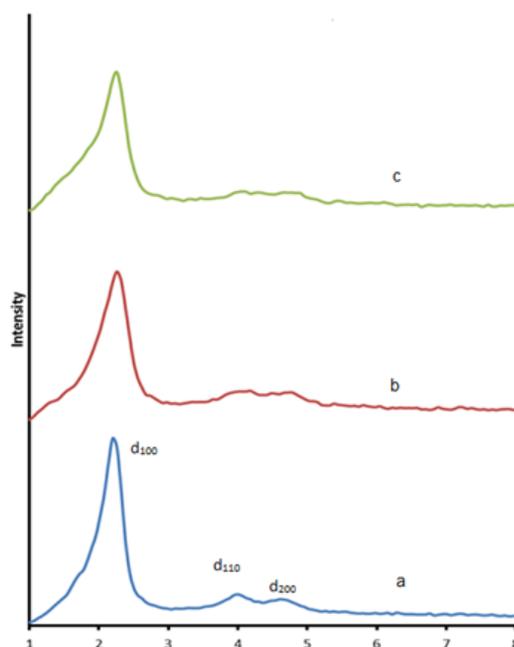


Fig. 2: Low angle X-ray diffraction patterns of (a) ZnO<sub>T</sub>/MCM, (b) ZnO<sub>W</sub>/MCM (c) ZnO<sub>E</sub>/MCM.

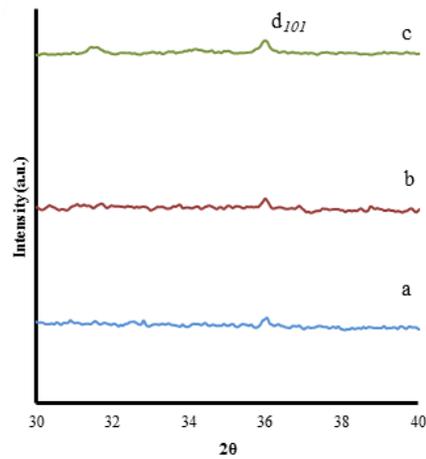


Fig. 3. High angle X-ray diffraction patterns of (a) ZnO<sub>T</sub>/MCM, (b) ZnO<sub>W</sub>/MCM (c) ZnO<sub>E</sub>/MCM.

As presented in figure 2 all three XRD patterns exhibit one intense diffraction peak (100) at about  $2.1^\circ$  and two minor peaks indexed as 110 and 200 in the region of  $4^\circ - 6^\circ$ , which are typical of MCM-41 mesoporous phase. Based on the patterns ZnO impregnated MCM-41 using THF has more uniform structures and pores compared with the other samples.

The high-angle XRD patterns of zinc incorporated samples show a peak on  $36.5^\circ 2\theta$  assigned to  $d_{101}$  reflection which indicates hexagonal zinc oxide crystals (Fig. 3).

### 3.2. Nitrogen physisorption

Nitrogen physisorption is a well-known technique for investigation of textural properties of porous materials. The nitrogen physisorption isotherm (figure 4) exhibits the type IV isotherm, which is the typical characteristic of mesoporous materials.

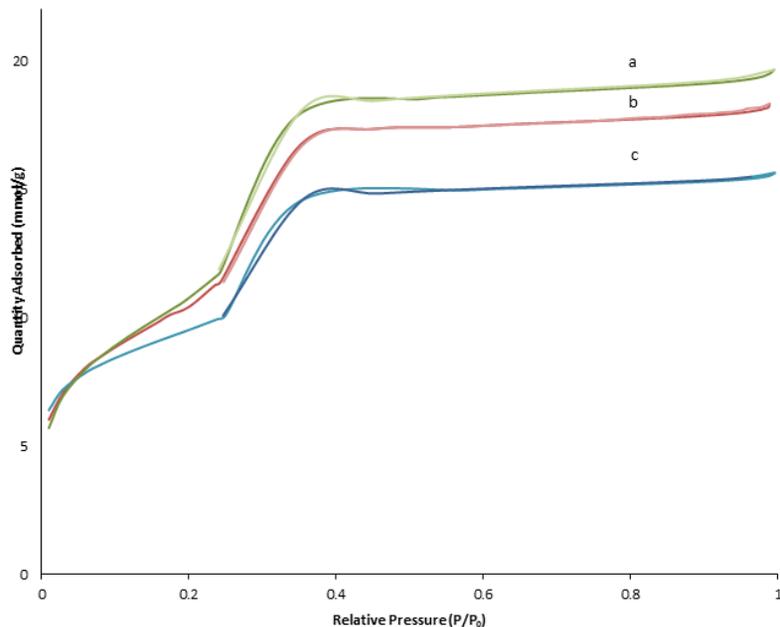


Fig. 4: Nitrogen physisorption patterns of a) ZnO<sub>T</sub>/MCM, b) ZnO<sub>W</sub>/MCM c) ZnO<sub>E</sub>/MCM.

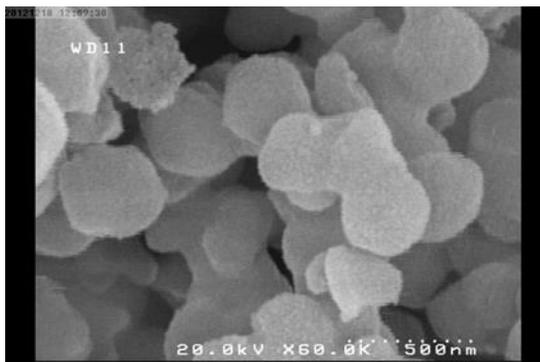


Fig. 5. SEM image of calcined MCM-41.

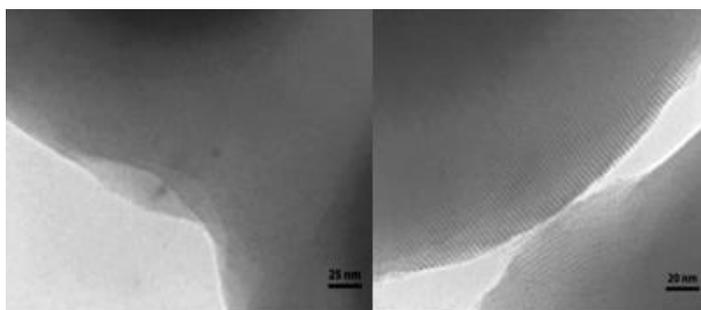
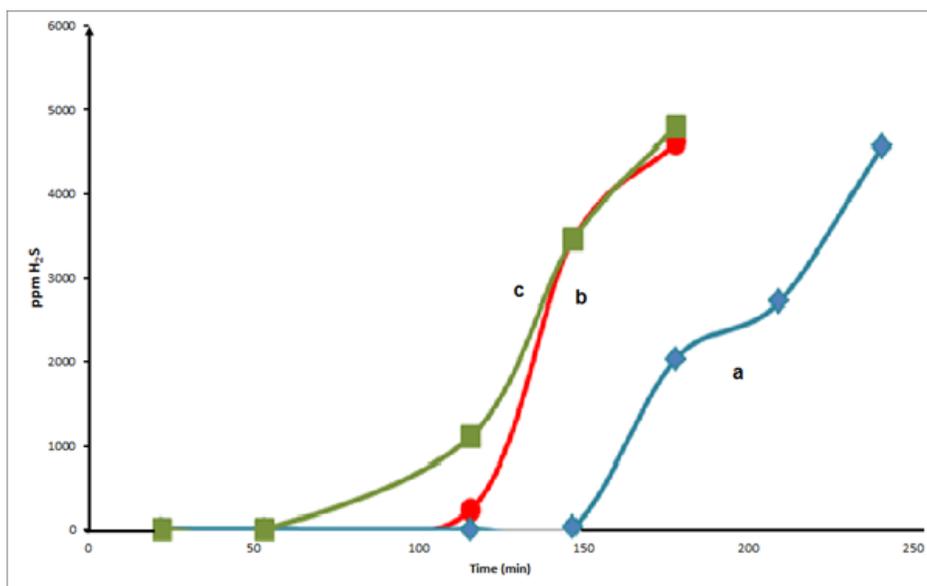


Fig. 6. HR-TEM images of MCM-41.

Specific surface area, calculated from the linear part of the Brunauer-Emmett-Teller (BET) equation (i.e.,  $P/P_0 \approx 0.05e^{0.25}$ ) was 1064, 986, 977.1 and 972  $m^2g^{-1}$  for calcined MCM-41,  $ZnO_T/MCM$ ,  $ZnO_W/MCM$  and  $ZnO_E/MCM$  respectively.

### 3.3. SEM

SEM image of MCM-41 (figure 5) presents that the particles size is in nanoscale.

Fig. 7: H<sub>2</sub>S adsorption breakpoints of a) ZnO<sub>T</sub>/MCM, b) ZnO<sub>W</sub>/MCM c) ZnO<sub>E</sub>/MCM

### 3.4. High resolution TEM

High Resolution TEM images of MCM-41 ( $x=0$ ) is shown in figure 5. Results show the high ordered hexagonal array of synthesized sample.

### 3.5. $H_2S$ adsorption

Synthesized samples showed high ability to remove  $H_2S$  at standard temperature. As presented in figure 7,  $ZnO_T/MCM$  showed better adsorption as expected. Operating conditions were in practical temperature of  $175\text{ }^\circ\text{C}$ , while space velocity in all the experiments was established on  $3000\text{ h}^{-1}$ .

## 4. Conclusion

Modification of silica mesoporous material, MCM-41, allows to introduce zinc into their pores by means of impregnation. Properties of zinc incorporated samples depend on some terms like solvent selection. Water is our most important solvent since it is essential for the survival. In this study the influence of solvent has been discussed and based on the samples characterization and  $H_2S$  adsorption results, THF is found to be a better precursor than water and ethanol.

Although drying of an impregnated support material appears to be very simple it should be noted that the conditions during drying can adversely influence the distribution of the precursor compound over the support material. This behavior is caused by solvent flows inside the pores of the support material during drying.

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