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

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ABSTRACT

The present work describes the use of mesoporous SBA-15 silica as support to disperse metal oxide nanophases, with the pores acting as nanoscale reactors. An original preparation method, called "Two solvents" technique [1], allows the production of Zinc oxide and Iron oxide based nanophases patterned by SBA-15 silica under mild conditions, with a preserved two-dimensional hexagonal structure. Zinc oxide as well as Iron oxide were highly dispersed into the well-ordered mesoporous silica channels forming a thin amorphous layer or small nanoparticles. In these nanosorbents the mesostructure was still retained together with a high surface area and large pore volume [2]. The MeO/SBA-15 nanosorbents have revealed a good performance in the H_2S gas removal compared with the commercial product. The confinement of the active phase in the SBA-15 structure enhances its ability to interact with hydrogen sulphide.

Keywords: SBA-15 silica, Sorbent, zinc oxide, iron oxide, H_2S removal.

1 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 [3]. 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 m^2/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 H_2S removal. In this framework, Hydrogen sulfide 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 [4]. 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. Under such conditions the nanostructure materials are stable, being the mesostructure retained up to high temperature, and they exhibit a higher reactivity toward H_2S in comparison with classical sorbents consisting of micrometer-sized particles.

2 RESULTS AND DISCUSSION

A simple and low cost novel strategy called "Two-Solvents" hexane-water impregnation procedure was employed. This method is based on a volume of metal precursor aqueous solution equal to the pore volume of host material. Second, the desired oxide is obtained *via* an appropriate thermal treatment. Once the nanocasting process is optimized, to understand the salient features of the nanophases crystallization upon calcination, various characterization technique were used. They revealed that metal oxides were highly dispersed into the well-ordered mesoporous channels. TEM micrographs show for the bare

SBA-15, a well-ordered 2D-hexagonal mesoporous symmetry (P6*mm*) with regular empty mesochannels with diameter of ca. 6–7 nm and walls thickness of about 4 nm (Figure 1).

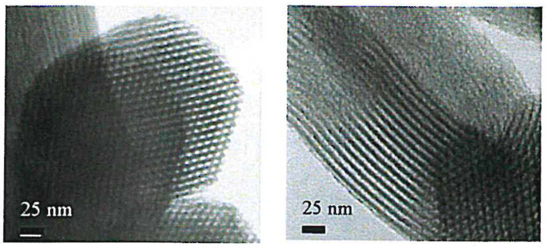

Figure 1. TEM images of bare mesostructured SBA-15

The sorbent performance for H_2S removal from a H_2S/He stream was investigated and compared with a commercial ZnO sorbent. The enhancement of H_2S removal capacity was attributed to the integration of the pore structure of mesoporous material and the promising desulfurization properties of both zinc and iron oxide. However, the iron-based nanosorbent shows 8 times higher capacity than the zinc-based one. The observed phenomenon can be attributed to the different kinetics of the active phases at the specific operative temperature (300 °C), confirming the suggestions reported in literature on pure phases. Moreover, the intrinsic H_2S removal with iron oxide produces multi-phase sulfides compared to the zinc oxide where a single phase sulfide is produced. A schematic graphical representation of the reaction process, and especially how the active metal oxide phase (zinc or iron oxide) is arranged into the mesopore channels of the silica support is shown in Figures 2 and 3.

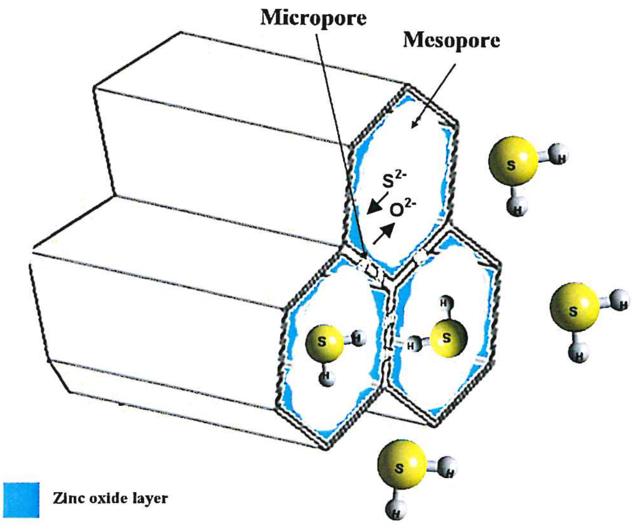

Figure 2. Schematic representation of the reaction process in the zinc oxide nanosorbent

Key issues for the viable use of a sorbent material are the feasibility of its regeneration after use and the maintaining of sulphur retention capacity during repeated sorption/regeneration cycles. In this context, the use of the SBA-15 silica support has improved the performance during the regeneration cycles and lowered the regeneration temperature due to a good dispersion and a minor sintering of the active phase. This behaviour has to be highlighted since represents a great advantage in view of the specific application.

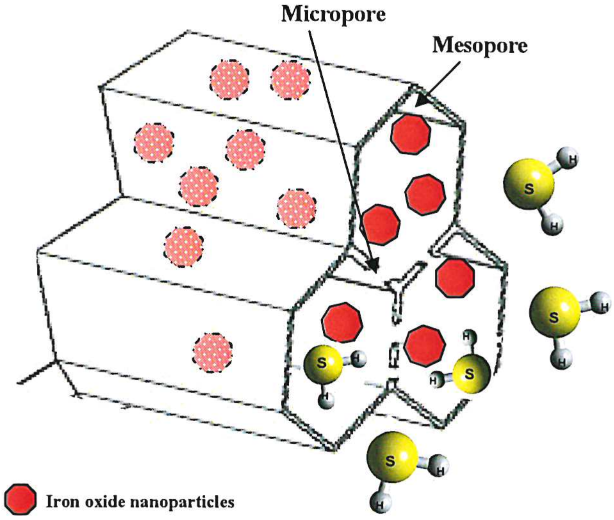

Figure 3. Schematic representation of the reaction process in the iron oxide nanosorbent

3 CONCLUSIONS

The overall results show: (i) the confinement of the active phase into the ordered channel system of mesostructured SBA-15 achieved by Two-Solvents impregnation strategy; (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; (iii) both sorbents show enhanced performance respect to the commercial ZnO unsupported sorbent being the sulphur retention capacity up to thirty times higher.

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